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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARD

RESEARCH PAPER RP1602

Part of Journal of Research of the National Bureau of Standards, Volume 33, September 1944

SOIL-CORROSION STUDIES, 1941: FERROUS AND NONFERROUS CORROSION-RESISTANT MATERIALS AND NONBITUMINOUS COATINGS

By Kirk H. Logan and Melvin Romanoff

ABSTRACT

The soil-corrosion investigation started in 1922 was intended to yield information on the corrosiveness of typical soils throughout the United States. The investigation of special materials and coatings begun 10 years later was intended primarily to assist manufacturers in the development of materials suitable for use in corrosive soils.

No attempt to secure specimens such that systematic data on the effect of individual alloying elements could be obtained was made but, manufacturers were invited to submit materials on which they desired information. Furthermore, the specimens were buried under simulated practical conditions, so that accurate technical control was not feasible. Also, since very few specimens of each type were included, dispersion of the data resulting from the general conditions of the tests makes it impossible to draw very definite conclusions with regard to the comparative merits of the several materials investigated. Nevertheless, the data give a general indication of what may be expected of a considerable variety of alloys when exposed to severe soil conditions. The addition of very small percentages of alloying elements does not have a marked effect on the rate of corrosion, but rather large percentages are apt to bring about a considerable improvement in corrosion resistance.

Steels high in nickel and chromium, and copper alloys high in copper are very resistant to nearly all soil conditions. Lead corrodes only slightly when a coating of an insoluble lead salt is deposited on the lead.

Bursting and crushing tests indicate that asbestos-cement pipe gained somewhat in strength from exposure to the soil for 4 years.

A 3-ounce coating of zinc adds about 3 years to the life of steel exposed to some of the most corrosive soils in the test sites. Lead coatings appear to be inadequate for severe soil conditions.

Several thick experimental coatings prevented practically all corrosion at most of the test sites for 9 years. Air-dried Bakelite coatings blistered within 4 years, but a baked-on Bakelite coating showed no change in appearance after 4 years except for a few blisters. Pitting occurred under some of these blisters. Most thin coatings blistered, became brittle, and within 4 years permitted rusting and pitting of the metal to which they were applied.

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I. INTRODUCTION

The studies of the effects of soils on materials used for underground pipes which the Bureau began in 1922, indicated that at least for the periods of exposure covered by the investigation, the maximum penetration of the materials by corrosion was approximately the same for the different commonly used ferrous materials [1].[1] Some ferrous alloys and some nonferrous alloys and metals appeared to be more resistant to the corrosive action of soils [2]. The investigation indicated also that rapid corrosion of the commonly used ferrous materials occurred under several soil conditions, and the conclusion [3] was reached that with respect to these materials the seriousness of the corrosion was largely controlled by the soil conditions to which the materials were exposed and nearly independent of the way in which the materials were made. It was shown that under most soil conditions the rate of maximum penetration of the metal decreased as the period of exposure increased [4]. The change in rate was attributed to changes in aeration and moisture as the soil in the trench settled, to a possible depletion of the corrosive elements in the soil adjacent to the specimens, and to the protective effect of the corrosion products.

Concurrent studies of bituminous protective coatings [5, 6, 7] indicated that this means of preventing corrosion was not entirely satisfactory partly because of the characteristics of the materials used and because of the difficulty of maintaining a complete and uninjured coating under the conditions to which it was usually subjected while the pipe line was being laid.

The original investigation [8] was, for the most part, limited to commonly used pipe materials and was intended to give comprehensive results on their reactions to typical soils throughout the United States. The results of this investigation stimulated an increased interest in the problem of discovering more effective ways of combating the destructive action of severely corrosive soils. A new investigation was undertaken in 1932 to study the effectiveness of

[1] Figures in brackets indicate the literature references at end of this paper.

corrosion-resisting pipe materials and the application of improved protective coatings. Fifteen different soils, most of which were known to be corrosive with respect to the commonly used irons and steels, were selected, and manufacturers were invited to submit specimens of materials which they believed or hoped would be resistant to the chosen soil conditions.

Since no attempt was made to secure specimens such that systematic data on the effect of individual alloying elements or their amounts could be obtained, the samples submitted differed in so many ways that in many cases it is impossible to explain observed differences in behavior. The mill scale was left on some of the materials because this condition represented the way the materials were normally used. Other materials were free from scale. There is some evidence that the mill scale affected the depth and distribution of the pits. In most cases the materials differed in more than one alloying element. In one case several materials differing in composition, and hence in electrical potential, were connected together to represent a common field condition. Some of the alloys and coatings were experimental. Others are at this time too expensive for ordinary underground use. Some commonly used pipe materials were buried as controls.

The above explanation should indicate to the reader that the term "corrosion resistant" may be inaccurate with respect to some of the materials reported on, and that the results of the tests do not represent the corrosiveness of soils in general.

It will be shown that some materials which corrode rapidly under some soil conditions are quite resistant to other corrosive soils.

Why pipes corrode when buried and why they corrode more in some soils than in others has not been fully determined. The commonly assigned cause of underground corrosion is a difference of potential between various points on the surface of the material. This difference may arise from lack of homogeneity of the metal, that is, the presence of mill scale, segregations, or the exposure of two different components of the materials, or from differences in the soil in contact with the material at different places. Soil solutions are usually too weak to account directly for the corrosion observed under most soil conditions. However, the electrical conductivity of the soils containing considerable quantities of soluble salts is an important factor in corrosion. Soil bacteria [9] have been shown to be a direct or indirect cause of corrosion in some soils.

The potential differences referred to are such that many investigators of corrosion have devoted most of their efforts to discovering why corrosion is not more serious. Their explanations [10, 11, 12, 13] deal largely with the character and distribution of corrosion products and with polarization resulting from the flow of corrosion currents.

The results of the corrosion tests reported in this paper should be interpreted with care because the conditions to which the specimens were exposed cannot be identical with those to which pipes of the materials tested may be subjected, because other conditions affecting the pipe may retard or increase the rate of corrosion, and because a pit of any chosen depth is more likely to be found on a large area (as that of a long pipe) than on a small one of the same material exposed to similar conditions.

The life of a pipe [14] can be estimated only indirectly and very roughly from the data to be presented, and that estimate will represent only the average life of a large number of pipes. The life of any individual pipe may be quite different from the average, just as the life of a person may be quite different from that of the average individual, as given in life-expectancy tables. Lack of exact reproducibility is characteristic of underground corrosion, especially with respect to pit depths, and in the discussion of the data presented in this paper attention will be called to instances in which the total pit depth for the period under discussion is less than the corresponding pit depth for a shorter period of exposure under nominally the same conditions. Final conclusions as to the corrodibility of the materials should therefore be withheld until all the specimens have been removed, which may be several years after the close of the present war. Nevertheless, the data are of considerable interest and value in that they indicate roughly the probable relative merits of several materials under several soil conditions and show the effects of the addition of alloying elements and suggest possibly helpful changes in the composition of pipe materials.

Conclusions based on the data on protective coatings should be drawn with even greater caution, since these coatings were applied under laboratory conditions that were probably much more favorable to good application than under commercial conditions, and because the coated specimens were handled with much greater care than it is practical to use with coated pipes. It is much easier to produce a perfect coating on a short piece of small-diameter pipe than on a long length of large-diameter pipe, and a coated-pipe line is subjected to destructive conditions not encountered by a small coated specimen. However, the data are of value for comparative purposes and indicate that considerable progress has been made in the art of pipe-line protection.

Perhaps a word of caution should be added regarding the use of averages with respect to underground corrosion. When a number of observations of the same thing are made, the results will not be identical because of imperfections in the methods and apparatus used. They should, however, be nearly alike, and an average of the results affords the best information concerning the measurements. However, when different things are measured, such as pit depths on the same materials in different soils, the average of the results yields little information as to what may be expected under any specific condition. For this reason such statements as the average life of pipe in the United States are of little value except from a statistical standpoint. For specific information, the performance of the material under consideration with respect to the soil conditions to be encountered must be known. Often these data are not available. In such cases analogous data may be considered, but it is seldom wise to use averages of data all of which were not obtained under the same conditions.

This report presents data on ferrous and nonferrous pipe materials and on nonbituminous pipe coatings removed in 1941 after exposures of approximately 2, 4, and 9 years. Other specimens of all but the 2-year-old materials have been removed and reported on in earlier publications [1, 2, 3, 15, 16, 17], and still others will be removed in the future.

II. PROPERTIES OF THE SOILS AT THE TEST SITES

As the character of the soil is the controlling factor in underground corrosion, information as to the characteristics of the soils at the test sites is essential to an understanding of the report. Most of this section of the paper is a reproduction of a similar section in Research Paper RP1460 [2]. Since that paper was written, it has been found that the pH values of certain soils when in their undisturbed condition are not the same as those of samples of the same soils after they have been aerated for some time [18]. The pH values given in table 1 were determined after the samples had been dried and pulverized, which is standard practice in the determination of the pH values of soils. When conditions permit, the pH values of all soils in the Bureau of Standards soil-corrosion investigations will be redetermined using soil in its natural condition. It is probable that this will result in some changes in the reported values for certain of the poorly aerated soils, since it has been found that aeration of these soils tends to lower their pH values. Attention is also called to the fact that the different soil horizons, or layers, sometimes differ widely in their physical and chemical properties, and hence in their corrosiveness. It follows that the data in this report are strictly applicable only to pipes buried in the soil horizons to which the specimens were exposed. In some soils, such as Rifle peat (soil 60), the peaty *B* horizon is underlain by a layer of clay at a depth of from 20 to 30 inches, and the two layers differ greatly in corrosiveness. Frequently large-diameter pipes are exposed to two soil horizons, and it seems probable that corrosion is accelerated because of a difference of potential between these horizons. Corrosion of large-diameter pipes may also be accelerated by differences in the aeration of the bottom and top of the pipe. It has been noted that the maximum pits frequently occur near the bottom of the pipe, where the aeration is poorest.

The nature of the soils at the test sites is indicated by the physical and chemical properties shown in table 1. The texture of the soils and their retentiveness of water is indicated relatively by values for the moisture equivalent, the quantity of water retained by a previously saturated soil against a centrifugal force of 1,000 times gravity. Since the true specific gravity of the mineral portion of soils varies within narrow limits, the apparent specific gravity, except in the case of organic soils, can be taken as a measure of their compactness and hence as a relative measure of their porosity. A soil having a very high moisture equivalent and a high apparent specific gravity, such as Acadia clay (soil 51), may be considered to be very fine in texture, highly retentive of water, very dense, and impermeable to the flow of air and water; this is confirmed by the aeration or drainage of the soil, which is poor. On the other hand, the fairly large value for the moisture equivalent (32 percent) of Hagerstown loam (soil 55), indicates this soil to be fairly heavy in texture and retentive of water. However, it is also very porous and well aerated, as indicated by the low value of its apparent specific gravity, 1.49.

Consideration of the chemical properties given in table 1 shows that the test sites represent a wide range of soil conditions. The range in pH is from 2.6 to 9.4, approximately the extreme limits shown by soils. The resistivity ranges from 62 to approximately 18,000 ohm-cm, corresponding to the concentration of sea water, on the one hand, to

TABLE 1.—*Properties of soils at the test sites*

Soil		Location	Aeration [1]	Moisture equivalent	Apparent specific gravity	Resistivity at 60° F (15.6° C)	pH	Total acidity, milligram equivalent per 100 g of soil	Composition of water extract—milligram equivalent per 100 g of soil						
No.	Type								Na+K As Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
				Percent		*Ohm-cm*									
51	Acadia clay	Spindletop, Tex	*P*	47.1	2.07	190	6.2	13.2	10.27	15.55	5.03	0.00	0.56	5.75	22.00
53	Cecil clay loam	Atlanta, Ga	*G*	33.7	1.60	17,794	4.6	9.6							
55	Hagerstown loam	Baltimore, Md	*G*	32.0	1.49	5,213	5.8	10.9							
56	Lake Charles clay	El Vista, Tex	*P*	28.7	2.03	406	7.1	4.5	3.12	0.69	0.47	.00	.80	1.59	3.04
58	Muck	New Orleans, La	*VP*	57.8	1.43	712	4.0	79.3	2.03	2.23	1.29	.00	.00	0.47	2.54
59	Carlisle muck	Kalamazoo, Mich	*VP*	43.6		1,659	5.5	33.3	1.03	3.08	2.70	.00	.00	3.47	1.04
60	Rifle peat	Plymouth, Ohio	*VP*	43.4	1.28	218	2.6	297.4	2.91	10.95	2.86	.00	.00	0.00	56.70
61	Sharkey clay	New Orleans, La	*P*	30.8	1.78	943	5.9	8.6	0.73	0.68	0.33	.00	.71	.10	0.91
62	Susquehanna clay	Meridian, Miss	*F*	34.6	1.79	6,922	4.1	24.2							
63	Tidal marsh	Charleston, S. C	*VP*	46.7	1.47	84	2.9	100.2	33.60	6.85	4.00	.00	.00	12.70	36.60
64	Docas Clay	Cholame, Calif	*P*	41.1	1.88	62	8.3	[2] *A*	28.10	2.29	0.76	.00	.89	28.80	0.26
65	Chino silt loam	Wilmington, Calif	*F*	26.4	1.41	148	7.2	*A*	7.65	12.40	2.20	.00	1.30	6.05	16.90
66	Mohave fine gravelly loam	Phoenix, Ariz	*G*	16.5	1.79	232	8.7	*A*	6.55	0.51	0.18	.00	0.73	2.77	2.97
67	Cinders	Milwaukee, Wis	*VP*	11.1		455	8.0	*A*	0.77	3.03	.53	.00	.55	0.08	2.89
69	Houghton muck	Kalamazoo, Mich	*VP*												
70	Merced silt loam	Buttonwillow, Calif	*F*	24.7	1.69	278	9.4	*A*	8.38	0.38	.22	.02	1.87	1.12	5.57

[1] Aeration of soils: *G*, good; *F*, fair; *P*, poor; *VP*, very poor.
[2] Alkaline.

the concentration of salts in a highly weathered soil, on the other. The soluble material in Rifle peat (soil 60), consists almost exclusively of sulfates. This soil is extremely acid, so much so that the soil actually contains sulfuric acid. In Docas clay (soil 64) the soluble material is almot entirely sodium chloride.

The names of the soils given in table 1 were assigned by the Soil Survey of the Bureau of Plant Industry of the United States Department of Agriculture. That part of the name which describes the texture of the soil refers to the texture of the uppermost, or *A*, horizon. As the specimens were buried at depths from 18 inches to 4 feet, they usually lie in the *B* or *C* horizon. As these horizons are frequently heavier in texture than the *A* horizon, the aeration of the soil in which the specimen lies may be poorer than is suggested by the soil types.

III. FERROUS MATERIALS

1. CAST MATERIALS

(a) DIMENSIONS AND COMPOSITION

Table 2 shows the composition and dimensions of the cast materials. The materials CB and CC were parts of a composite specimen consisting of a piece of deLavaud cast iron bolted to a piece of charcoal cast iron by means of a charcoal cast-iron bolt (CD) and a steel bolt (CE).

TABLE 2.—*Dimensions and composition of cast materials*

Material	Identification	Year buried	Form	Nominal width or diameter	Length	Thickness
				in.	*in.*	*in.*
Charcoal [1] cast iron	CB	1939	Plate	3.5	12	0.375
deLavaud [1] [2] cast iron	CC	1939	do	3.5	12	.50
Rattled [3] cast iron	G	1932	Pipe	1.25	13.5	.250
Sand-coated cast iron	F	1932	do	1.25	13.5	.250
Low-alloy cast iron	I	1932	do	1.25	12	.350
Do	J	1932	do	1.25	12	.350
Do	C	1932	do	1.5	12	.250
High-alloy cast iron	E	1932	do	1.5	10	.250

Material	C			Si	Mn	S	P	Cr	Ni	Cu
	Free	Combined	Total							
	%	%	%	%	%	%	%	%	%	%
Charcoal [1] cast iron	------	------	2.40	0.95	0.95	0.065	0.17	------	------	1.00
deLavaud [1] [2] cast iron	------	3.70	------	1.51	.38	.071	.78	------	------	------
Rattled [3] cast iron	2.94	0.64	3.58	1.64	.48	.074	.79	------	------	------
Sgpd-coated cast iron	2.94	.64	3.58	1.64	.48	.074	.79	------	------	------
Low-alloy cast iron	------	------	2.53	1.43	.28	.077	.128	------	------	.51
Do	------	------	2.90	2.04	.83	.060	.248	------	------	.62
Do	3.00	.50	3.50	2.50	.70	.050	.400	0.30	0.15	------
High-alloy cast iron	------	------	2.98	2.13	1.00	------	------	2.61	15.00	6.58

[1] The deLavaud and charcoal cast-iron plates were connected by means of a charcoal cast-iron bolt (CD) and a steel bolt (CE).
[2] Curved plate cut from 12-in. class 150 Super deLavaud pipe.
[3] Ordinary iron horizontally cast in green sand molds and rattled to remove sand.

(b) SPECIMENS EXPOSED FOR 9 YEARS

Tables 3 and 4 show the losses of weight and the depths of maximum pits for the cast specimens exposed approximately 9 years. The maximum pit depth recorded in table 4 is the average of the deepest pit on each of the two specimens of 1¼-inch pipe about 1 foot long. It will be noted that in approximately 10 percent of the cases in table 3 and in 30 percent of the cases in table 4, the average loss of weight or the average depth of the maximum pits was less for the 9-year-old specimens than for the corresponding 7-year-old ones. In most of these cases the single maximum value was also greater for the earlier removals. This lack of reproducibility of the data is characteristic of underground corrosion and may be attributed to lack of homogeneity in the material under test, in the soil, or in the conditions of the test. In other words, the specimens examined were not sufficiently large to constitute adequate or representative samples, especially with respect to maximum pit depth. Studies of the relation between the maximum pit depth and the magnitude of the area from which the maximum pit depth was selected [14] indicate that the area would have to be very large before a deeper pit could not be expected to occur on a larger area. Because of this characteristic of the data on maximum pit depths, comparison of the depths of maximum pits on individual specimens should be made with caution.

TABLE 3.—*Loss of weight of cast-iron pipe exposed for 9 years*

[In ounces per square foot [a]]

Soil		Exposure	Horizontally cast in sand mold, *G*	Low-alloy					High-alloy *E*
						I+*J*			
No.	Type			*I*	*J*	Average	Standard error	*C*	
		Years							
53	Cecil clay loam	9.47	3.25	2.76	2.55	2.66	0.2	2.25	1.35
55	Hagerstown loam	9.11	3.55	2.67	[b] 2.10	2.38	.2	2.04	[c] 0.72
56	Lake Charles clay	9.42	[d] *D*(42)	37.34	33.71	35.52	3.0	29.70	14.62
58	Muck	9.51	20.08	24.05	27.10	25.58	1.0	21.88	9.91
59	Carlisle muck	9.12	[b] [e] 3.60	4.08	[b] 2.92	3.50	0.4	[e] 2.37	0.66
60	Rifle peat	9.24	20.77	[e] 18.15	[e] 17.01	17.58	4.2	[e] 13.07	[e] 10.00
61	Sharkey clay	9.53	7.08	7.54	6.89	7.22	0.4	7.21	2.33
62	Susquehanna clay	9.47	8.10	6.61	6.37	6.49	.9	6.92	2.73
63	Tidal marsh	9.55	6.14	[e] 9.98	[e] 11.40	10.69	3.5	2.56	1.63
64	Docas clay	9.21	*D*(34)	46.83	44.59	45.71	0.8	[bf] 41.93	12.82
65	Chino silt loam	9.25	7.62	11.04	10.28	10.66	.8	14.61	[e] 2.55
66	Mohave fine gravelly loam	9.23	[b] 3.96	8.22	12.15	10.18	1.3	10.74	[ee] 3.29
67	Cinders	9.24	*D*	[g] 61.41+	[g] 64.99+	63.20	.....	45.74	52.33

[a] Each ounce per square foot corresponds to an average penetration of 0.0017 inch.
[b] Average loss of weight of 1939 removals is greater. The maximum loss of weight of the individual specimens of the 1939 removals is greater.
[c] Average loss of weight of 1939 removals is greater. The maximum loss of weight of the individual specimens of the 1941 removals is greater.
[d] *D*, both specimens destroyed. The number in parentheses is the approximate loss of weight.
[e] Loss of weight of individual specimens differed from each other by more than 50 percent.
[f] Data for 1 specimen only.
[g] Data for 1 specimen only. The other specimen was destroyed by corrosion.

TABLE 4.—*Depths of maximum penetration on cast-iron pipe exposed for 9 years*

[In mils]

Soil		Horizontally cast in sand mold					Low alloy						High-alloy
				F+G					*I+J*				
No.	Type	*F*	*G*	Average	Standard deviation	Standard error	*I*	*J*	Average	Standard deviation	Standard error	*C*	*E*
53	Cecil clay loam	[a] [b] 75	[b] 57	66	20	12	58	62	60	15	8	[a] [b] 66	[b] 33
55	Hagerstown loam	[b] 98	[c] 123	110	22	13	108	[a] [c] 96	102	38	22	123	[b] 34
56	Lake Charles clay	[d] 250+(7)	250+(7)	250+			[c] 249	[c] 215	232	43	25	[c] 216+	[c] 58
58	Muck	[c] 250+(7)	[c] 250+(5, 7)	250+			240	[c] 233	236	38	22	250+	[b] [c] 53
59	Carlisle muck	[c] 44	52	48	12	7	74	[c] 49	62	20	12	24	[b] 26
60	Rifle peat	[a] [c] 163+	[a] [c] 175+	169+	81	47	[c] 140	[c] 130	135	75	43	[a] [c] 93	[a] [c] 45
61	Sharkey clay	78	78	78	5	3	113	80	96	24	14	119	[c] 36
62	Susquehanna clay	[b] 90	[a] [b] 81	86	23	13	[b] 91	[a] [b] 63	77	23	14	[c] 80	53
63	Tidal marsh	131	114	122	22	13	[c] 104	85	94	16	9	[b] 40	[a] [b] 32
64	Docas clay	250+	250+	250+			317+	[c] 246	282+	41	24	[c] [f] 250+	74
65	Chino silt loam	145	131	138	27	16	172	156	164	24	14	[c] 161	[b] 35
66	Mohave fine gravelly loam	[b] 118	[b] 152(7)	135	22	13	214	[b] 193	204	23	13	[b] 141	40
67	Cinders	250+(5, 7)	250+(5, 7)	250+			[c] 327+(5)	[b] [c] 266+(5, 7)	296+	69	40	[b] [c] 195+(5, 7)	[c] 250+(5, 7)

[a] Maximum pit depths of individual specimens differed from each other by more than 50 percent.
[b] Averabe pit depths of the 1939 removals are greater. The single maximum pit depths of the 1939 removals are greater.
[c] Average pit depths of the 1939 removals are greater. The single maximum pit depths of the 1941 removals are greater.
[d] The plus (+) sign indicates that 1 or both specimens were punctured. A number in parentheses after the pit depth indicates that 1 or both specimens of a previous removal was punctured, e. g., (2) indicates a puncture after 2 years, etc.
[e] Uniform corrosion (no reference surface) on 1 or both specimens.
[f] Data for 1 specimen only.

To provide a more reliable basis for comparing materials and soils, tables 5 to 8 have been prepared. The data for all the periods of exposure from 12 soils were used in compiling these tables, soils 51, 57, and 67 having been excluded on account of insufficient data or the destruction of the specimens because of the extreme corrosiveness of the soils. In table 5 the average loss of weight for all the materials in all the soils was obtained for each period of exposure. This average was used as a reference for presenting the individual losses for each material in each of the soils on a relative percentage basis for that particular period. The results for the four periods of exposure were then averaged to form table 6. This permits comparisons of the materials in each soil and of the corrosiveness of each soil with respect to each material. Tables 7 and 8 were prepared for the maximum penetrations in the same way as tables 5 and 6 were prepared for the loss of weights.

TABLE 5.—*Relative loss of weight of cast specimens based upon the average loss of all specimens for each period*

[In percent]

Soil No.	2-year exposure [a]					5-year exposure [b]				
	G [c]	*I*	*J*	*C*	*E*	*G*	*I*	*J*	*C*	*E*
53	83	54	54	68	21	30	25	27	29	11
55	47	49	69	60	13	35	22	32	22	9
56	167	90	90	127	59	221	142	187	156	69
58	103	82	65	160	15	180	186	171	214	71
59						38	34	37	28	6
60	187	174	138	159	74	104	108	107	100	74
61	19	17	18	22	5	72	84	93	71	27
62	119	116	119	113	29	84	63	68	69	16
63	67	49	81	55	10	48	42	54	26	8
64	222	273	281	254	78	326	398	399	466	47
65	182	211	194	228	27	92	121	138	182	45
66	106	89	106	146	54	92	81	105	167	45
Average	118	109	110	127	35	110	109	117	128	36

Soil No.	7-year exposure [c]					9-year exposure [d]				
	G	*I*	*J*	*C*	*E*	*G*	*I*	*J*	*C*	*E*
53	29	19	20	19	8	27	22	21	18	11
55	35	27	28	23	8	29	22	17	17	6
56	252	283	260	224	108	343	305	275	242	119
58	217	236	229	206	99	164	196	221	179	81
59	44	34	37	25	7	29	33	24	19	14
60	56	83	65	49	15	170	148	139	107	83
61	52	61	61	57	19	58	62	56	59	19
62	57	49	55	28	11	66	54	52	57	22
63	16	40	34	24	8	50	82	93	21	13
64	406	451	505	512	66	278	383	364	343	105
65	82	92	103	127	23	62	90	84	119	21
66	64	54	87	69	41	32	67	99	88	27
Average	109	119	124	114	34	109	122	120	106	47

[a] Average loss=5.66 ounces per square foot.
[b] Average loss=6.69 ounces per square foot.
[c] Average loss=8.73 ounces per square foot.
[d] Average loss=12.24 ounces per square foot.
[e] See table 2 for the composition of the materials.

TABLE 6.—*Average of the relative loss of weight of the cast materials for four periods of exposure.*

[In percent]

Soil No.	*G* [a]		*I*		*J*		*C*		*E*		Average
	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	
53	42	14	30	8	30	9	34	11	13	2	30
55	36	5	30	6	34	14	30	10	9	2	28
56	246	36	205	53	203	42	187	28	89	14	186
58	166	24	175	33	172	37	190	11	67	18	154
59 [b]	37	4	34	0	33	3	24	3	22	16	25
60	129	31	128	21	112	18	104	22	61	16	107
61	50	12	56	14	57	15	52	11	18	4	47
62	82	13	70	16	74	15	67	17	20	3	63
63	45	11	53	10	66	12	32	7	10	1	41
64	308	39	376	38	387	47	394	58	74	12	256
65	104	27	128	29	130	24	164	26	29	6	111
66	74	16	73	7	99	6	118	22	42	5	81
Average	110		113		116		116		38		

[a] See table 2 for composition of the materials.
[b] Data for only 3 periods of exposure.

TABLE 7.—*Relative maximum penetration of cast specimens based upon the average maximum penetration of all specimens for each period*

[In percent]

Soil No.	2-year exposure [a]						5-year exposure [b]					
	F [c]	*G*	*I*	*J*	*C*	*E*	*F*	*G*	*I*	*J*	*C*	*E*
53	100	87	62	112	81	62	71	73	68	65	58	52
55	100	100	58	75	54	62	95	72	81	85	83	53
56	85	75	46	62	66	87	171	157	141	134	145	46
58	71	54	85	58	91	163	150	258	154	157	179	49
59							75	48	62	50	16	20
60	104	108	79	79	71	50	86	98	72	82	104	115
61	50	89	62	54	31	75	69	79	120	86	63	56
62	145	133	207	141	166	89	95	137	102	115	109	71
63	79	50	41	106	21	46	62	107	86	120	17	23
64	272	257	282	249	295	58	167	181	150	150	210	39
65	95	104	116	120	120	54	107	135	137	144	131	60
66	116	124	118	112	141	54	102	114	86	101	173	52
Average	111	107	105	106	103	67	104	122	105	107	107	53

Soil No.	7-year exposure [c]						9-year exposure [d]					
	F	*G*	*I*	*J*	*C*	*E*	*F*	*G*	*I*	*J*	*C*	*E*
53	103	71	50	60	89	51	60	46	47	50	53	26
55	127	127	91	98	96	41	79	99	87	82	99	27
56	252	252	192	185	151	53	201	201	200	173	173	47
58	201	252	193	180	177	58	201	201	193	187	201	43
59	46	52	44	57	20	28	35	42	59	39	19	21
60	35	26	81	25	18	22	131	140	112	104	75	36
61	56	76	91	78	53	30	63	63	91	64	96	29
62	107	119	95	84	83	37	72	65	73	51	64	43
63	52	61	91	72	133	55	105	91	83	68	32	26
64	151	123	147	157	144	40	201	201	254	197	201	59
65	87	113	111	119	129	42	116	105	138	125	129	128
66	123	182	150	201	162	38	95	122	172	155	113	32
Average	112	121	104	110	104	41	113	115	126	108	104	85

[a] Average maximum pit depth = 48 mils.
[b] Average maximum pit depth = 69 mils.
[c] Average maximum pit depth = 99 mils.
[d] Average maximum pit depth = 125 mils.
[c] See table 2 for composition of the materials.

TABLE 8.—*Average of the relative maximum penetration of the cast materials for the four periods of exposure*

[In percent]

Soil No.	F [a]		G		I		J		C		E		
	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Average
53	84	9	69	9	57	15	72	14	70	9	48	7	67
55	100	11	100	10	79	11	85	5	83	10	46	7	82
56	177	35	171	38	145	35	138	29	134	23	58	10	137
58	156	30	191	48	156	26	146	29	162	24	63	14	146
59 [b]	52	12	47	11	55	6	49	3	18	3	23	2	41
60	89	20	93	24	86	9	72	17	67	18	56	6	77
61	60	5	77	4	91	12	70	9	61	18	48	10	68
62	105	15	115	13	119	30	98	19	106	21	60	12	100
63	74	13	77	14	75	12	92	11	51	27	38	7	68
64	198	26	190	29	208	35	188	23	212	32	49	5	174
65	101	8	114	8	126	3	127	6	127	5	46	7	107
66	109	6	136	14	132	23	142	23	147	14	44	5	118
Average	109	------	115	------	111	------	107	------	103	------	48	------	------

[a] See table 2 for the composition of the materials.
[b] Data for only 3 periods of exposure.

An analysis of the data in tables 5 and 7 indicates that the high-alloy cast iron, *E*, is definitely superior with respect to loss of weight and pitting to the other cast irons in all the soils The data also show that, except in a very few cases, there are no real, consistent differences in the loss of weight or maximum penetration between any of the plain or low-alloy cast irons. It will be noted that for all the periods the low-alloy cast iron, *C*, is consistently better than the other low-alloy or plain cast iron in soil 59 with respect to loss of weight and maximum penetration; and that plain cast iron, *G*, is consistently better than the others in soil 64 and 65 with respect to loss of weight only. The summary of the relative values in tables 6 and 8 shows that with respect to loss of weight the composite averages of all periods for the plain or low-alloy cast irons agree within 6 percent, and with respect to pitting, the composite averages of all periods for the same materials agree within 12 percent It is doubtful that the small differences can be considered significant in view of the standard error of the averages. Hence, the data bring out the fact that none of the plain or low-alloy cast irons is definitely superior, in general, to the other materials in the 12 soils tested. Figure 1 shows the specimens of cast iron removed from Mohave fine gravelly loam (soil 66) after 9 years of exposure.

(c) SPECIMENS EXPOSED FOR 2 YEARS

The cast-iron specimens exposed for 2 years consist of 12 by 3½ by ½-inch sections of 12-inch class 150 Super deLavaud pipe bolted to flat 12 by 3½ by ⅜-inch charcoal cast-iron plates by means of steel and charcoal cast-iron bolts.

Table 9 indicates that the charcoal cast iron lost more weight than the Super deLavaud iron in most soils, and in all but one soil the maximum pit depths on the Super deLavaud cast iron were definitely less

FIGURE 1.—*Cast-iron specimens exposed to soil 66 for 9 years.*

F, Sand-coated; *G*, rattled; *I*, low-alloy; *J*, low-alloy; *C*, low-alloy; *E*, high-alloy.

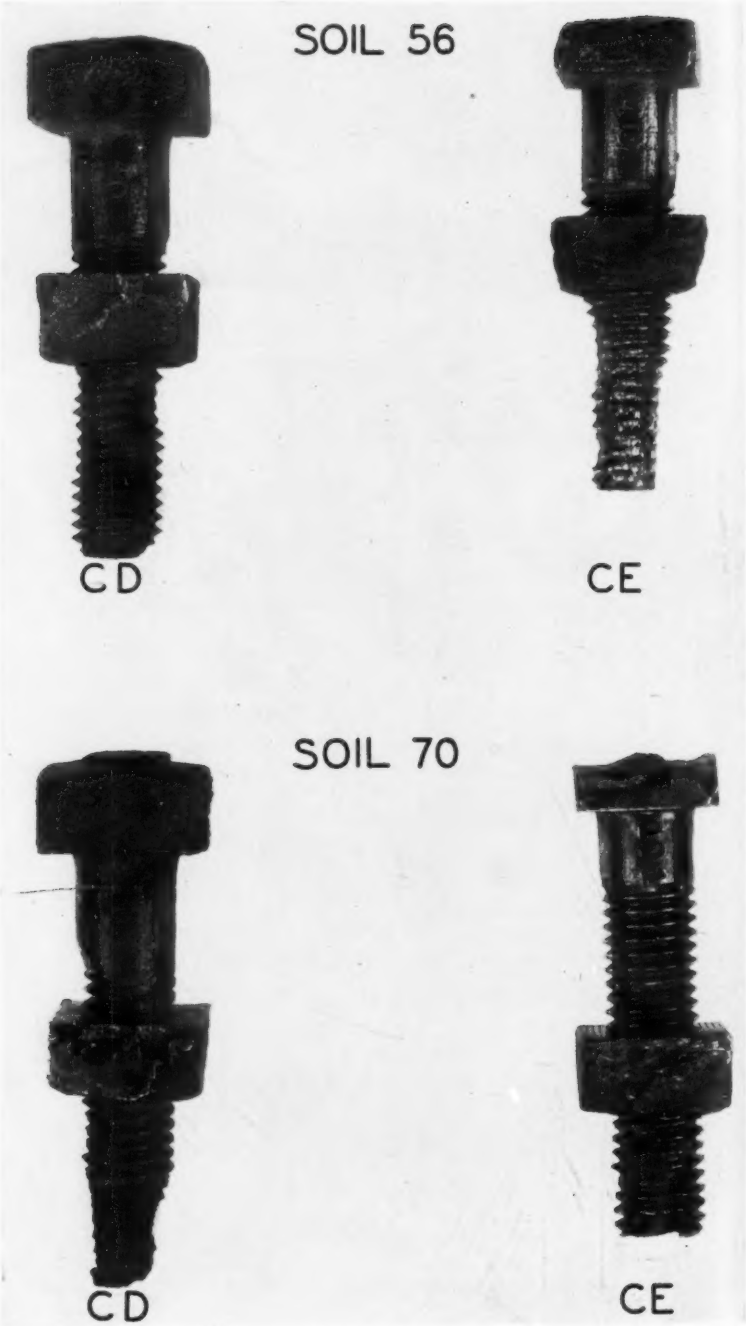

FIGURE 2.—*Charcoal cast iron (CD) and steel (CE) bolts exposed to both soil 56 and 70 for approximately 2 years each.*

than on the charcoal cast iron. This might be attributed to galvanic action between the different metals in addition to the other causes of corrosion. Figure 2 shows the condition of the cast-iron and steel bolts which were connected to the couples in soils 56 and 70.

TABLE 9.—*Loss of weight and depth of maximum penetration of cast-iron plates and cast-iron and steel bolts (the plates were connected by the bolts)*

[Exposure 2 years]

Soil		Exposure	deLavaud cast iron		Charcoal cast iron		Nuts and bolts	
							Steel	Charcoal cast iron,
			CC		*CB*		*CE*	*CD*
No.	Type		Loss of weight	Maximum penetration	Loss of weight	Maximum penetration	Loss of weight	Loss of weight
		Years	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*oz/ft²*
53	Cecil clay loam	1.91	1.21	30	1.59	38	1.92	1.81
55	Hagerstown loam	2.03	1.03	32	1.05	68	1.28	1.56
56	Lake Charles clay	1.91	6.13	45	11.27	74	20.10	9.04
58	Muck	1.91	5.98	42	4.10	58	6.47	7.12
60	Rifle peat	1.91	4.27	23	3.21	41	5.06	3.32
61	Sharkey clay	1.92	1.66	36	2.56	58	2.54	2.28
62	Susquehanna clay	1.90	2.52	34	2.73	57	2.57	3.31
63	Tidal marsh	1.88	1.94	36	2.69	57	(a)	(a)
64	Docas clay	1.90	4.53	36	4.64	57	3.28	[b] 5.54
65	Chino silt loam	1.91	1.89	34	3.39	54	4.24	3.85
66	Mohave fine gravelly loam	1.86	4.88	34	6.28	54	(a)	(a)
67	Cinders	1.90	18.48	88	20.67	102	16.22	18.18
69	Houghton muck	1.90	2.25	38	2.08	36	1.71	1.86
70	Merced silt loam	1.90	7.40	96	10.50	122	[b] 11.19	10.12

[a] Both specimens missing.
[b] Loss of weight for individual specimens differed from each other by more than 50 percent.

Laboratory measurements were made on the open-circuit differences of potential between a pair of the two different cast-iron plates buried in a box containing a saturated sample of Lake Charles clay (soil 56). The difference of potential reached the constant value of 61 millivolts after several weeks, the deLavaud specimen being cathodic. This is in accord with the data for soil 56 reported in table 9, which shows the loss of weight on the charcoal cast iron to be almost twice the loss on the Super deLavaud specimen. The pitting was also deeper on the charcoal cast iron. If it be assumed that the losses of weight due to the soil conditions alone were about the same for the two materials, the difference in corrosion observed in table 9 might be accounted for by the extra galvanic action caused by the dissimilarity between the two metals. As the charcoal cast iron was anodic, its tendency to corrode was greater. However, the deLavaud cast iron will not be cathodic in all soils, since the two types of cast iron would probably fall in the same group of the galvanic series set up by McKay and Worthington [19], who arranged the metals in groups according to their tendency to corrode galvanically, and showed that the relative positions of metals in the same group are subject to reversals. Such a reversal was observed on another set of measurements of a pair of the cast-iron materials in Docas clay (soil 64). The metals were buried in a very wet sample of the soil. The deLavaud cast iron was cathodic at first, but after considerable drying of the soil, a reversal

took place and the Super deLavaud plate become anodic to the charcoal cast iron.

This shows that the environmental condition of the soil in which couples are buried plays an important role in corrosion due to galvanic action. The aeration of a soil is affected by its retentiveness of water, and since the aeration and water content vary from season to season, it cannot be forecast which part of a couple whose constituent metals fall within the same group of the galvanic series will become cathodic or anodic. As the possibility of a reversal taking place has been shown to exist, this should be taken into consideration when combinations of metals which might give rise to galvanic action are to be buried.

2. WROUGHT MATERIALS

(a) DIMENSIONS AND COMPOSITION

Table 10 shows the dimensions and composition of the wrought ferrous specimens. It will be noted that some of the mill scale was left on the puddled wrought-iron pipes buried in 1932 and that a hard, black mill scale covered the entire surface of the copper-nickel steel and the nickel-copper steel plates buried in 1937. The other specimens did not have any mill-scale coating. The losses of weight and depths of pits of specimens exposed for short periods are affected by the mill scale, which acts as an inperfect protective coating and stimulates local galvanic corrosion. Most of the scale is lost after a few years' exposure, an effect which probably becomes of less importance as the test continues.

(b) SPECIMENS EXPOSED FOR 9 YEARS

1. *Specimens of Pipe.*—Table 11 shows the losses of weight of the wrought ferrous pipe buried in 1932 and removed in 1941. In most soils the low-carbon steel, *N*, seems to lose a little more weight than most of the other materials, but usually the differences are not great, except with respect to the specimens high in chromium.

Table 12 shows the averages of the deepest pits on the specimens of wrought pipe exposed 9 years. As was said in the discussion of the corresponding cast specimens, data on the maximum pit depths are too erratic to justify comparisons of materials unless a considerable number of specimens of each material is available. As an example, the data in table 12 show that corrosion had punctured the wall of seven of the pipes removed after 7 years of exposure, but that other specimens of the same materials were not punctured even after 9 years of exposure to the same soils. For the purpose of determining whether the data showed any real difference in loss of weight and in resistance to pitting for all periods of exposure, tables 13 to 16 were prepared according to the method used in constructing tables 5 to 8. In addition to the soils omitted from those tables for the cast materials, soils 64 and 66 were excluded from tables 13 to 16, since most of the specimens contained punctures in the last two removals. It was permissible to use these data for these two soils for the cast materials because of the greater wall thickness of the pipes. Tables 13 and 14 indicate that for all periods, with respect to loss of weight the 5-percent chromium steel (*P*) is consistently better than any of the other specimens in soils 53 and 55, and nickel-copper steel (*D*) is consistently best in soil 65. With respect to pitting, *D* is consistently better than the other specimens in soil 53.

TABLE 10.—*Composition of wrought ferrous materials*

Material	Identification	Year buried	Form	Nominal width or diameter	Length	Thickness	C	Si	Mn	S	P	Cr	Ni	Cu	Mo	Other elements
WROUGHT IRON																
				in.	*in.*	*in.*	%	%	%	%	%	%	%	%	%	%
Hand-puddled	*A*[a]	1932	Pipe	1.5	12	0.145	0.016	0.10	0.029	0.018	0.160	------	------	------	------	Oxide + slag, 2.56.
Roe process	*B*[a]	1932	do	1.5	12	.145	.017	.125	.041	.018	.106	------	------	------	------	Oxide + slag, 2.681.
CARBON STEELS																
Low-carbon steel	*N*	1932	Pipe	2.3	10	0.145	0.15	------	0.49	0.030	0.013	------	------	------	------	
LOW-ALLOY IRONS AND STEELS																
Open-hearth steel	*A*	1937	Plate	2.5	12	0.188	0.033	0.002	0.029	0.017	0.006	0.049	0.034	0.052	------	
Copper-molybdenum open, hearth iron.	*MM*	1939	do	2.5	12	.250	.04	------	.16	.027	.008	.04	.14	.051	0.07	O_2, 0.015; N_2, 0.008; Sn, 0.002.
Do	*O*	1937	do	2.5	12	.243	.03	.003	.16	.032	.007	.02	.15	.45	.07	
Do	*N*	1937	do	2.5	12	.250	.06	.001	.098	.029	.069	.02	.14	.54	.13	
Do	*H*	1932	Pipe	1.5	12	.145	.04	.05	.32	.027	.016	------	------	.52	.15	
Copper-nickel steel	*J*[b]	1937	Plate	2.5	12	.265	.06	.047	.49	.025	.095	------	.52	.95	------	
Nickel-copper steel	*B*[b]	1937	do	2.5	12	.248	.07	.14	.44	.022	.010	------	1.96	1.01	------	
Do	*D*	1932	Pipe	1.5	12	.145	.14	.19	.21	------	------	------	2.47	1.08	------	
Chromium - silicon - copper - phosphorus steel.	*C*	1937	Plate	2.5	12	.188	.075	.84	.20	.018	.124	1.02	.022	.428	------	
2% chromium steel with molybdenum	*NN*	1939	Pipe	1.5	14.5	.145	.09	.25	.46	.010	.015	1.96	------	------	.49	
Do	*KK*	1937	Plate	2.5	12	.175	.082	.51	.46	.015	.017	2.01	.07	.004	.57	

[a] These specimens had some mill scale on the surface at time of burial.
[b] These specimens were completely covered with a hard, black mill scale at time of burial.

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TABLE 10.—*Composition of wrought ferrous materials*—Continued

Material	Identification	Year buried	Form	Nominal width or diameter	Length	Thickness	C	Si	Mn	S	P	Cr	Ni	Cu	Mo	Other elements
				in.	*in.*	*in.*	%	%	%	%	%	%	%	%	%	%
CHROMIUM STEEL																
4 to 6% chromium steel	*P*	1932	Pipe	2.3	10	0.154	0.13	------	0.46	0.025	0.012	5.05	------	------	------	
Do	*D*	1937	Plate	2.5	12	.245	.077	0.43	.37	.005	.015	5.02	0.09	0.008	------	
4 to 6% chromium steel with molybdenum.	*E*	1937	...do	2.5	12	.188	.074	.41	.32	.006	.013	4.67	.09	.004	0.51	Al, 0.030; Ti, 0.022.
Do	*H*	1937	...do	2.5	12	.203	.060	.39	.40	.014	.021	5.76	.17	.004	.43	Al, 0.27.
12% chromium steel	*U*	1932	...do	4	6	.063	.065	.28	.38	.017	.011	11.95	.482	.025	------	
18% chromium steel	*V*	1932	...do	4	6	.063	.070	.34	.36	.015	.014	17.08	.092	.021	------	
Do	*X*	1932	Pipe	1.5	12	.145	.12	.277	.42	.017	.016	17.72	.287	------	------	
HIGH-CHROMIUM NICKEL AND MANGANESE STEELS																
18% chromium steel with nickel	*K*	1932	Plate	3	11	0.025	0.08	0.33	0.44	0.022	0.015	17.20	8.95	------	------	
Do	*R*	1932	Pipe	1.5	12	.145	.05	.28	.46	.011	.015	17.52	8.85	------	------	
Do	*W*	1932	Plate	4	6	.063	.093	.42	.36	.017	.008	18.69	9.18	0.016	------	
18% chromium steel with nickel and manganese.	*T*	1932	...do	6	10	.063	.06	.40	6.09	------	------	17.76	3.83	.95	------	
Do	*S*	1932	...do	6	10	.063	.07	.48	9.44	------	------	17.78	------	.74	------	
18% chromium steel with nickel, manganese, and molybdenum.	*CM*	1939	...do	2	12.5	.25	.07	.40	1.24	.008	.016	17.78	10.96	------	2.63	
22% chromium steel with nickel and manganese.	*Y*	1932	...do	4	6	.063	.144	.59	1.80	.011	.015	22.68	12.94	.021	------	
22% nickel-chromium steel with manganese and molybdenum.	*DT*	1939	...do	2.5	12	.25	.07	.91	1.99	.012	.014	19.27	22.12	1.07	3.52	

TABLE 11.—*Loss of weight of wrought pipe exposed for 9 years*

[In ounces per square foot] [a]

Soil		Wrought iron				Cu-Mo open-hearth iron	Low-carbon steel	Alloy steel			
No.	Type	Hand puddled	Mechanically puddled	*A+B*				2.5% Ni 1.1% Cu	5% Cr	18% Cr	18% Cr 8% Ni
		A	*B*	Average	Standard error	*H*	*N*	*D*	*P*	*X*	*R*
53	Cecil clay loam	3.72	3.70	3.71	0.3	3.99	[b] 4.09	[b] 2.53	[b] 2.24		
55	Hagerstown loam	3.68	3.78	3.73	.1	[b] 3.19	3.82	[b] 2.05	1.92		
56	Lake Charles clay	[e] 22.83	19.54	21.18		[e] 18.93	28.76	16.69	23.58		
58	Muck	12.57	12.68	12.62	.5	14.51	16.24	[b] 6.55	13.88	(d)	0.022
59	Carlisle muck	2.44	2.34	2.39	.4	[b] 2.37	4.70	[b] 2.61	2.76		
60	Rifle peat	[e] 14.26	[e] 16.48	15.37	4.8	13.68	16.72	[e] 10.28	15.55		
61	Sharkey clay	6.42	[b] 5.66	6.04	.6	5.56	5.78	[b] 3.37	5.10		
62	Susquehanna clay	7.80	9.38	8.59	1.1	7.02	6.65	5.42	4.64	0.012	.0029
63	Tidal marsh	[e] 8.52	4.24	6.38	1.9	6.33	[e] 9.03	7.58	[e] 5.85	[e] 1.33	(d)
64	Docas clay	[f] 16.00+	[f] 18.35+	17.18+		[g] *D*	*D*	[b e] 24.79	*D*	(d)	.059
65	Chino silt loam	13.60	11.44	12.52	.9	15.05	[h] 12.86	[b] 6.00	[b] 10.91		
66	Mohave fine gravelly loam	[b e] 5.82	[b] 9.99	7.90		14.60	18.56	[e h] 7.54	18.32		
67	Cinders	[f] 15.21+	*D*	15.21+		*D*	[f] 58.39+	*D*	27.92	[e] 1.46	.0023

[a] Each ounce per square foot corresponds to an average penetration of 0.0015 inch.
[b] Average loss of weight of 1939 removals is greater. The maximum loss of weight for the individual specimens of the 1939 removals is greater.
[c] Data for 1 specimen only.
[d] Data cannot be used because of abnormal corrosion due to the presence of asphalt on the ends of the specimen.
[e] Data for the individual specimens differed from the average by more than 50%.
[f] Data for 1 specimen only. The other specimen was destroyed by corrosion.
[g] *D*, both specimens destroyed by corrosion.
[h] Average loss of weight of 1939 removals is greater. The maximum loss of weight for the individual specimens of the 1941 removals is greater.

TABLE 12.—*Depths of maximum pits on wrought pipe exposed for 9 years*

[In mils]

Soil		Wrought iron				Cu-Mo open-hearth iron	Low-carbon steel	Alloy steel			
No.	Type	Hand puddled	Mechanically puddled	*A+B*				2.5% Ni 1.1% Cu	5% Cr	18% Cr	18% Cr 8% Ni
		A	*B*	Average	Standard error	*H*	*N*	*D*	*P*	*X*	*R*
53	Cecil clay loam	[a] 50	[b] 73	62	9	[c d] 109+	59	[a] 37	70		
55	Hagerstown loam	[a] 60	84	72	8	93	59	62	[a] 84		
56	Lake Charles clay	[a c] 96	[a f] 106(7)	101		[c] 145+(7)	154+(7)	145+(7)	[a] 136(5, 7)		
58	Muck	113	116	117	10	[a] 96(7)	110	[a] 52(7)	111	[a g] 10	8
59	Carlisle muck	2	28	30	4	[d] 22	[d] 40	14	20		
60	Rifle peat	[d] 55	[d] 64	60	16	[d] 61	[d] 27	[d] 38	110		
61	Sharkey clay	61	[d] 86	74	16	82	[d] 96	[a] 41	74		
62	Susquehanna clay	[d] 72	[d] 101	86	22	[d] 86	[d] 87	[b d] 58	[a] 70(7)	< 6	< 6
63	Tidal marsh	100	[d] 55	78	19	[b d] 67	[a] 54	[d] 70	136+	[c] 112	[a g] 26
64	Docas clay	[b] 120+(7)	145+(7)	132+	12	145+(7)	154+(5, 7)	[c] 145+(7)	154+(5, 7)	[g] 96	[d] 36
65	Chino silt loam	[a] 102(7)	110	106(7)	6	[a] 106	112	74	[b] 131+(7)		
66	Mohave fine gravelly loam	[a c] 88	[b] 130+(7)	109+		145+(5, 7)	154+(5, 7)	[b d] 96+(7)	154+(7)		
67	Cinders	145+(5, 7)	145+(5, 7)	145+		145+(5)	154+(2, 5, 7)	145+(5, 7)	125+(5)	84	6

[a] Average pit depths of the 1939 removals are greater. The single maximum pit depth of the 1939 removals is greater.

[b] Average pit depths of the 1939 removals are greater. The single maximum pit depth of the 1941 removals is greater.

[c] The plus sign (+) in all cases indicates that 1 or both specimens were punctured.

[d] The maximum pit for individual specimens differed from each other by more than 50%.

[e] Data for 1 specimen only.

[f] A number in parentheses after the pit depth indicates that 1 or both specimens of a previous removal was punctured, e. g., (2) indicates a puncture after 2 years, etc.

[g] Deeper pits present because of abnormal corrosion due to the presence of asphalt on the ends of the pipe. These pits have not been included in the data.

TABLE 13.—*Relative loss of weight of wrought specimens based upon the average loss of all specimens for each period*

[In percent]

Soil No.	2-year exposure [a]						5-year exposure [b]					
	A [c]	*B*	*H*	*N*	*D*	*P*	*A*	*B*	*H*	*N*	*D*	*P*
53	104	103	83	80	65	41	50	57	53	57	41	38
55	85	86	59	72	50	34	44	45	35	42	26	23
56	105	132	69	121	100	75	207	145	168	266	98	157
58	105	96	87	96	105	55	187	199	199	213	147	142
59	.....	.....	.....	.....	.....	.....	35	30	32	45	32	38
60	170	150	146	187	146	129	121	131	111	210	150	223
61	39	37	29	24	35	23	107	94	78	76	49	63
62	90	120	111	122	81	72	77	76	79	90	44	50
63	90	79	75	115	47	40	59	46	58	87	43	70
65	238	184	224	222	149	216	142	139	214	196	80	186
Average	114	110	98	115	86	76	103	96	103	128	71	99

Soil No.	7-year exposure [d]						9-year exposure [d]					
	A	*B*	*H*	*N*	*D*	*P*	*A*	*B*	*H*	*N*	*D*	*P*
53	50	51	58	63	39	36	42	42	45	46	28	25
55	52	50	51	48	32	25	41	42	36	43	23	22
56	257	220	196	314	146	270	257	220	213	323	188	265
58	179	174	184	211	146	176	141	143	163	183	74	156
59	31	27	39	45	44	34	27	26	27	53	29	31
60	77	81	67	114	57	43	160	185	154	188	116	175
61	94	96	73	85	57	76	72	64	63	65	38	57
62	90	90	76	80	55	52	87	105	79	75	61	52
63	51	52	72	106	62	62	96	48	71	102	85	66
65	136	132	221	206	91	201	153	129	169	145	67	123
Average	102	97	104	127	73	98	108	100	102	122	71	97

[a] Average loss of weight=3.34 ounces per square foot.
[b] Average loss of weight=5.23 ounces pre square foot.
[c] Average loss of weight=6.67 ounces per square foot.
[d] Average loss of weight=8.90 ounces per square foot.
[e] See table 10 for the composition of the materials.

TABLE 14.—*Average of the relative loss of weights of wrought specimens for the four periods of exposure*

[In percent]

Soil No.	*A* [a]		*B*		*H*		*N*		*D*		*P*		Average
	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	Relative loss	Standard error	
53	62	14	63	14	60	8	62	6	43	8	35	4	54
55	56	9	56	10	45	6	51	8	33	6	26	3	44
56	206	37	179	24	162	31	256	47	133	21	192	46	188
58	153	19	153	22	158	25	176	27	118	18	132	27	148
59 [b]	31	2	28	1	33	1	48	3	35	5	34	4	35
60	132	21	137	21	120	19	175	20	117	22	142	39	137
61	78	15	73	14	61	11	62	14	45	4	55	11	62
62	86	3	98	9	86	9	92	10	60	8	56	7	80
63	74	11	56	8	69	4	102	8	59	10	60	5	70
65	167	26	146	13	207	14	192	18	97	18	182	19	165
Average	104	.....	99	.....	100	.....	122	.....	74	.....	91	.....	.....

[a] See table 10 for the composition of the materials.
[b] Data for only 3 periods of exposure.

TABLE 15.—*Relative maximum penetration of wrought specimens based upon the average maximum penetration of all specimens for each period*

[In percent]

Soil No.	2-year exposure [a]						5-year exposure [b]					
	A [e]	*B*	*H*	*N*	*D*	*P*	*A*	*B*	*H*	*N*	*D*	*P*
53	97	86	154	106	66	131	115	127	117	90	47	101
55	114	120	171	117	91	120	142	151	135	102	61	117
56	63	68	57	57	57	165	118	117	117	127	75	270
58	57	51	60	51	66	103	122	115	108	185	127	130
59	.....	.....	.....	.....	.....	.....	45	32	9	36	5	27
60	68	68	77	106	80	94	68	66	38	43	47	130
61	48	29	40	29	34	29	74	66	106	97	54	66
62	140	200	205	177	120	148	97	101	154	118	83	140
63	80	46	86	43	68	123	39	66	88	65	31	156
65	154	188	268	114	117	194	163	156	174	133	86	192
Average	91	95	124	89	78	123	98	100	105	100	62	130

Soil No.	7-year exposure [c]						9-year exposure [d]					
	A	*B*	*H*	*N*	*D*	*P*	*A*	*B*	*H*	*N*	*D*	*P*
53	108	107	129	76	62	80	63	92	137	74	47	66
55	98	84	96	80	72	124	76	106	117	74	78	106
56	127	149	157	176	204	217	121	133	183	194	183	171
58	118	155	204	155	155	98	149	146	121	138	65	146
59	25	21	14	42	20	28	40	35	28	50	18	21
60	42	48	22	24	20	87	69	81	77	34	48	120
61	62	70	91	89	72	53	77	108	103	121	52	91
62	97	110	110	100	101	176	91	127	108	110	73	80
63	90	55	145	98	58	125	126	60	84	68	88	171
65	155	149	165	117	96	194	128	138	133	141	93	165
Average	92	95	113	96	86	118	94	104	109	100	74	110

[a] Average maximum pit depth, 35 mils.
[b] Average maximum pit depth, 56 mils.
[c] Average maximum pit depth, 71 mils.
[d] Average maximum pit depth, 79 mils.
[e] See table 10 for the composition of the materials.

TABLE 16.—*Average of the relative maximum penetrations of wrought specimens for the four periods of exposure*

[In percent]

Soil No.	*A* [a]		*B*		*H*		*N*		*D*		*P*		Average
	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	Relative maximum penetration	Standard error	
53	96	11	103	9	134	9	86	9	56	2	100	11	96
55	108	13	115	15	130	15	93	10	76	5	117	4	104
56	107	15	117	17	128	28	138	31	130	37	207	26	126
58	112	18	117	23	123	30	132	29	103	23	117	9	117
59 [b]	37	5	29	3	17	6	43	1	14	5	37	10	30
60	62	6	66	6	54	13	52	18	49	12	110	11	66
61	65	7	68	17	85	24	84	20	53	8	60	14	69
62	106	12	134	23	144	23	126	18	94	11	140	19	124
63	84	17	59	5	101	14	68	12	61	12	144	11	86
65	150	8	158	9	185	29	126	8	98	7	186	8	138
Average	93	.....	97	.....	110	.....	95	.....	73	.....	122	.....	.....

[a] See table 10 for the composition of the materials.
[b] Data for only 3 periods of exposure.

Figure 3, which has been prepared from the averages in tables 14 and 16, indicates that with respect to the relative average values of all materials in the 10 soils for the 4 periods of exposure, nickel-copper steel (*D*) is better with respect to pitting and loss of weight. However, it should be noted that the mill scale had been removed from these specimens prior to burial. This might have had an efffect on the pitting, as will be shown in a later section when the data of this nickel-copper steel are compared with the data of a steel of a similar

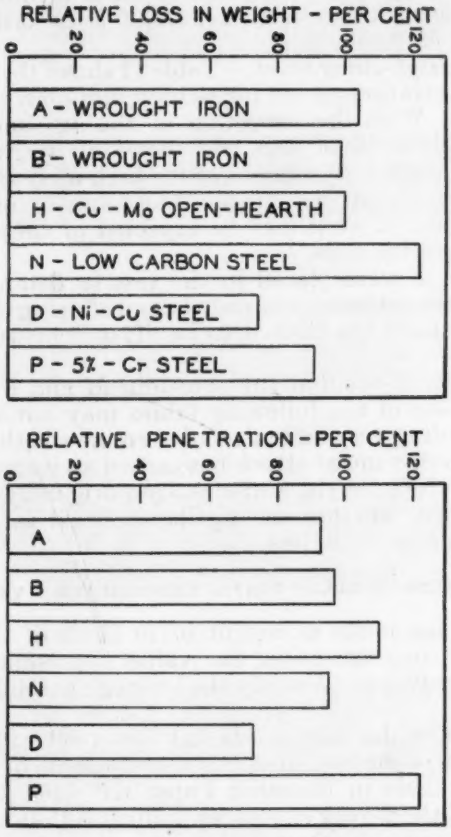

FIGURE 3.—*Relative loss of weight and maximum penetration of wrought ferrous materials.*

composition from which the mill scale had not been removed. Figure 3 also shows that although the 5-percent chromium steel (*P*) is superior to ordinary steel with respect to loss of weight, it is inferior with respect to pitting. This may be accounted for by the formation of an adherent chromic-oxide film on the surface of the alloy, which is largely cathodic and behaves temporarily as a protective coating. But with the breaking down of this film locally, the resulting differences in potential between the small anodic areas and the cathodic surface tend to cause an acceleration of pitting. Since the rate of corrosion of ferrous metals in soils is usually determined chiefly by

the rate at which the cathode is depolarized, the relatively large cathodic area would be expected to support a comparatively high rate of pitting. Figure 4 shows the wrought pipe buried in Susquehanna clay (soil 62) for 9 years.

As was pointed out in the introduction, such figures as figure 3, which are based on the averages of the performances of materials that do not behave the same in different soils, have limited value, since the material which shows the best average performance may not be the best for some specific soil condition. This is illustrated by the performance of the nickel-copper steel (*D*) for the last two periods of exposure in soil 56 (table 15).

2. *Specimens of High-Alloy Sheet.*—Table 17 shows the loss of weight and maximum penetration of six high-chromium-alloy sheets after 9 years of exposure. With the exception of the 12- and 17-percent-chromium materials in three soils, the losses of weight and the pit depths were very small. Specimens of the high-alloy sheet buried in soil 64 for 9 years are shown in figure 5, The behavior of these specimens is characteristic of what may be expected of these materials in poorly aerated, corrosive soils.

Materials *S* and *T* were placed in the test to determine whether manganese could be used instead of nickel as an alloying element. The number of specimens is too limited to justify a conclusion regarding this.

It should be pointed out that the notations *M* and *U* appearing in table 12 and in some of the following tables may not represent real differences. It is often very difficult to determine whether a specimen is unaffected or whether metal attack has caused an increased roughening of the surface, because the surfaces were originally rough before burial. In any case, whether the pitting is listed as *M* or *U*, the amount of corrosion is negligible.

c) SPECIMENS OF ALLOY PLATES EXPOSED FOR 4 YEARS

Table 18 shows the losses of weight of 10 kinds of alloy iron and steel plates With one exception, the values represent the average loss of weight of two plates. Usually the losses do not differ more than 15 percent.

Apparently most of the alloy steels lost less weight than the open-hearth steel in most of the test sites, but a comparison of table 12 with the corresponding table in Research Paper RP 1460 [2], which reports the results of the 2-year exposures, indicates that, although as a whole the performance of the materials was consistent for the two periods, there are a number of cases where the data are inconsistent. Table 19 shows the averages of the deepest pits on these materials. In general, the alloys seem to pit less deeply than plain steel in most of the test sites, but more deeply in several of them.

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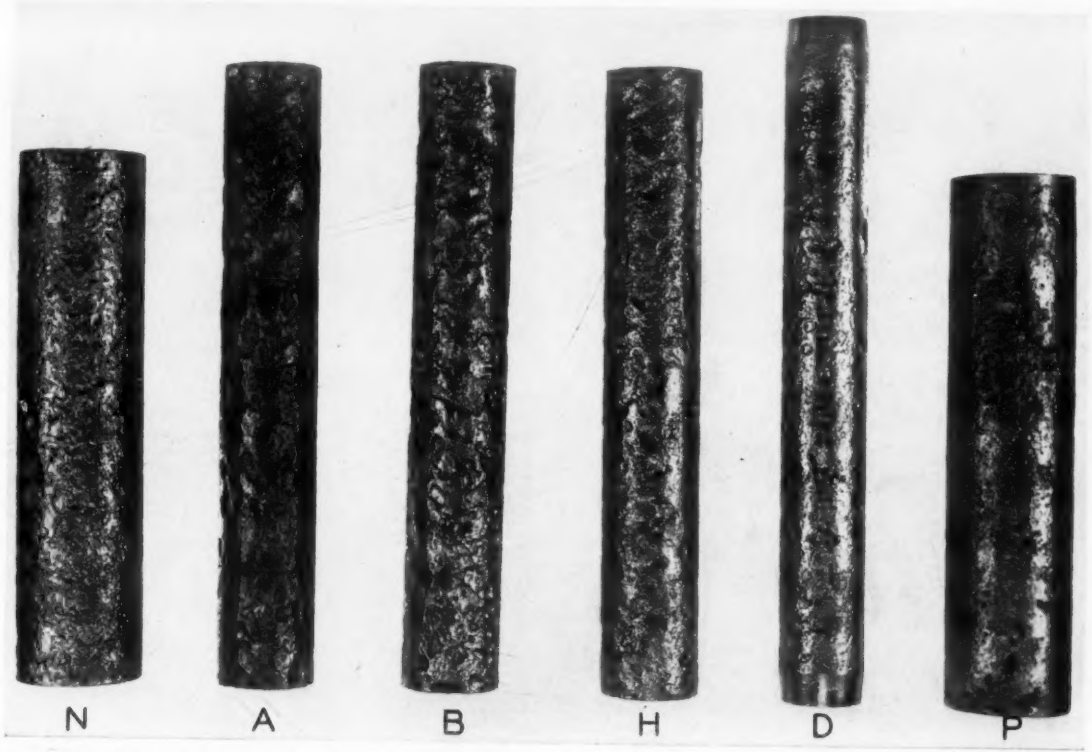

FIGURE 4.—*Wrought-iron and steel pipe buried 9 years in Susquehanna clay at Meridian, Miss. (soil 62).*

N, Low-carbon tube; *A*, hand-puddled wrought iron; *B*, machine-puddled wrought iron; *H*, copper-molybdenum open-hearth iron; *D*, nickel-copper steel; *P*, 5-percent-chromium steel.

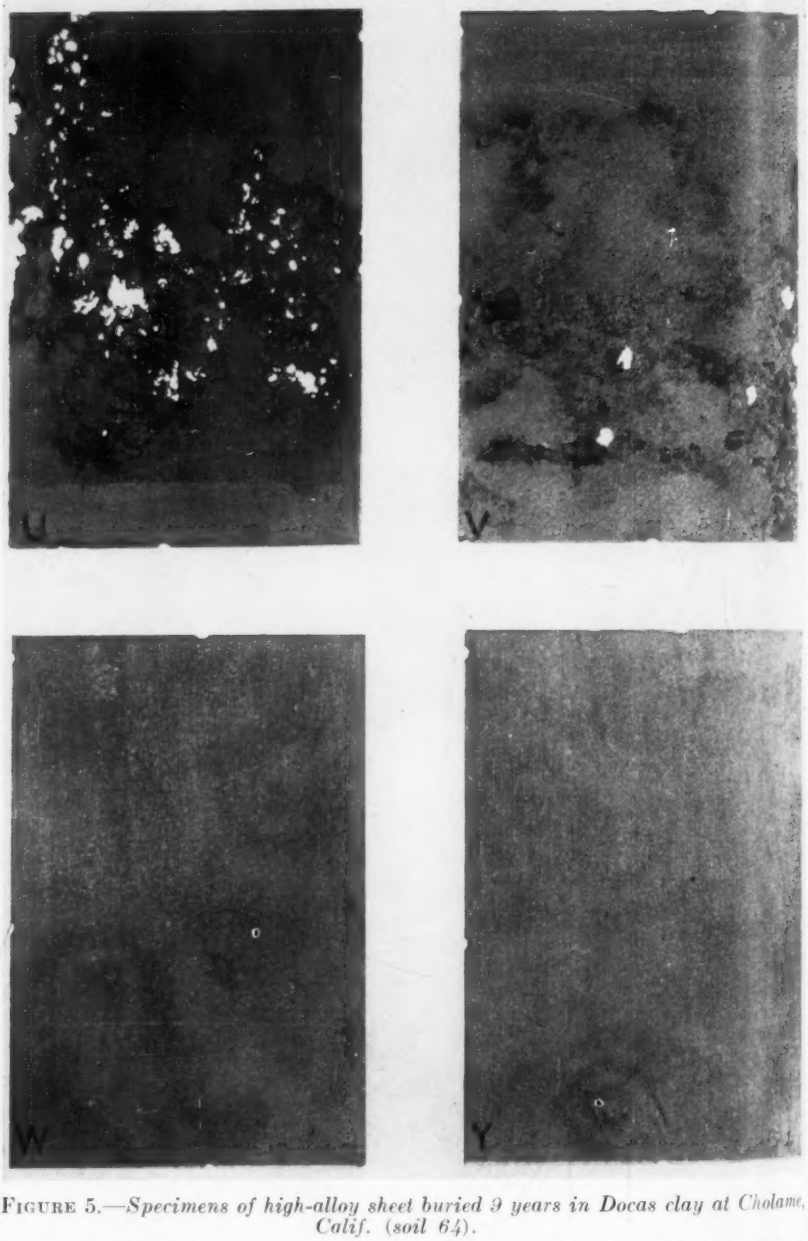

FIGURE 5.—*Specimens of high-alloy sheet buried 9 years in Docas clay at Cholame, Calif. (soil 64).*

U, 12-percent-chromium steel; *V*, 18-percent chromium; *W*, 18-percent-chromium steel with nickel; *Y*, 22-percent-chromium steel with nickel and manganese. The white spots on specimens *W* and *Y* are not holes.

TABLE 17.—*Average loss of weight and maximum penetration of high-alloy steel sheets exposed for 9 years*

TABLE 17.—*Average loss of weight and maximum penetration of high-alloy steel sheets exposed for 9 years*

M, shallow metal attack, roughening of surface, but no definite pitting.
P, definite pitting, but no pits greater than 6 mils.
U, apparently unaffected by corrosion.
+, one or more specimens contained holes because of corrosion, rendering the computation of the exact penetration impossible. The thickness of the specimen has been used as the maximum pit in this case.

Soil No.	(5) [a] 11.95% Cr 0.48% Ni .38% Mn		(5) 17.08% Cr 0.09% Ni .36% Mn		(2) 17.72% Cr 9.44% Mn		(1) 17.76% Cr 3.83% Ni 6.09% Mn		(2) 17.2% Cr 8.95% Ni 0.44% Mn		(5) 18.69% Cr 9.18% Ni 0.36% Mn		(5) 22.68% Cr 12.94% Ni 1.50% Mn	
	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average	Loss, average	Maximum penetration, average
	U		*V*		*S*		*T*		*K* [b]		*W*		*Y*	
	oz/ft²	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*
53									0.0010	*U*				
55	0.00042	*M*	0.0014	*U*							0.00053	*P*	0.0015	*P*
56									[c].110	[d] [c] 25+(5,7)				
58									.0011	*U*				
59	.00084	*P*	.0016	*P*					.0014	*M*	.00074	*P*	.0021	*P*
60	[d].0019	[d] *P*(5,7)	[f].15	[f] *P*(5)					.0012	*M*(5)	.0012	*P*	.0024	*P*
61									.0016	*P*				
62									.0011	*M*				
63														
64	3.17	63+(2,5,7)	1.12	63+(2,5,7)	0.48	63+(2,5,7)	0.44	[d] *P*(2,7)	[f].077	[f] 14+	.0026	*P*	.0062	*P*
65	0.040	53+(2,7)	[f] 0.24	[d] [f] 43+(2,5,7)					.0014	[d] *P* (2,7)	.0015	*P*(2)	.0020	*P*(2)
66	.56	55+(2,5,7)	.70	63+(7)					[f].25	[f] 14+(5,7)	.00053	*M*	[f].12	[f] 14+
67					.00066	[d] *M*(7)	.0042	*M*	.0015	*P*				

[a] The number in parentheses indicates the number of specimens removed from each test site.
[b] Polished surface.
[c] Data for 1 specimen only.
[d] Average loss of weight or pit depth of 1939 removal is greater.
[e] The number in parentheses after the pit depth indicates that at least 1 specimen of a previous removal was punctured, e. g., (2) indicates a puncture after 2 years.
[f] Data for the individual specimens differed from each other by more than 50 percent.

TABLE 18.—*Loss of weight of alloy iron and steel plates exposed for 4 years*

[In ounces per square foot]

Soil		Exposure	Open-hearth steel	Open-hearth iron		Low-alloy steel				4 to 6% chromium steel			High alloy steel
				0.45% Cu .07% Mo	0.54% Cu .13% Mo	0.95% Cu .52% Ni	1.01% Cu 1.96% Ni	Cr-Si-Cu-P steel 1.02% Cr	2.01% Cr 0.57% Mo	5.02% Cr	4.67% Cr 0.51% Mo .030% Al .022% Ti	5.76% Cr 0.43% Mo .027% Al	18% Cr
No.	Type		*A*	*O*	*N*	*J*	*B*	*C*	*KK*	*D*	*E*	H_1	H_3
		Years											
53	Cecil clay loam	4.01	3.23	2.90	3.02	1.32	1.07	2.41	2.18	1.31	1.59	1.44	.....
55	Hagerstown loam	3.90	2.58	2.78	2.73	1.81	1.22	2.33	2.38	1.12	1.19	1.06	.....
56	Lake Charles clay	3.99	18.38	13.79	17.37	19.17	19.52	20.76	14.48	17.93	16.26	14.32	.....
58	Muck	4.01	9.88	9.87	9.36	10.65	11.01	9.03	8.36	5.93	7.16	[c]6.81	[a]0.6
60	Rifle peat	3.98	9.52	7.36	8.22	8.62	9.55	10.23	6.00	6.64	6.23	6.24	.....
61	Sharkey clay	4.01	5.40	5.61	5.65	4.82	3.94	4.59	4.67	1.57	1.81	1.64	.....
62	Susquehanna clay	4.00	3.71	3.62	3.68	3.31	2.94	3.05	2.99	1.22	1.09	1.28	.....
63	Tidal marsh	4.01	[c]6.23	4.70	4.69	3.46	3.44	4.14	3.12	3.80	5.15	5.41	.....
64	Docas clay	3.98	7.44	8.03	[c]6.63	[c]5.95	[c]4.86	5.12	5.39	[c]4.35	5.11	[c]5.03	.....
65	Chino silt loam	3.99	5.26	5.00	5.03	5.00	5.04	5.44	4.53	[c]2.15	[c]2.09	[c]2.17	.....
66	Mohave fine gravelly loam	3.95	[a]16.82	11.65	11.96	10.38	11.38	13.56	12.26	12.13	12.04	14.53	.....
67	Cinders	3.98	34.27	[c]33.22	27.70	35.06	44.29	[c]13.92	[c]16.45	[b]18.09	[b][c]11.69	[b]12.88	.....
69	Houghton muck	3.98	4.21	2.86	2.90	2.61	2.37	2.54	2.46	0.86	0.77	0.72	.....
70	Merced silt loam	3.98	10.63	[b]11.02	[b]10.25	[b]7.62	7.80	9.80	9.67	[b]10.04	9.88	10.25	.....

[a] Data for 1 specimen only.
[b] Data for the individual specimens differ from each other by more than 50%.
[c] Average loss of weight of the 1939 removals is greater.

TABLE 19.—*Maximum penetration of alloy iron and steel plates exposed for 4 years*

Table 20 and figure 6 show the relative losses of weight and pit depths for the materials in all soils based on data for two periods of exposure. The table indicates that in corrosive soils in general the low-alloy materials lose less weight but are not superior to open-hearth steel with respect to pit depths. A possible explanation of this condition is that the corrosion products tend to form an imperfect protective coating which sometimes accelerates corrosion at the weak points.

The behavior of the 4- to 6-percent chromium steel in this test is in agreement with the behavior of the 5-percent chromium steel specimens in the 9-year test, where lower loss of weight and deeper pitting was observed in comparison to plain steel.

Further inspection of figure 6 shows that the nickel-copper steel (*B*) is no better than some of the other low-alloy steels with respect to loss of weight and pitting. This is contrary to the results of the 9-year specimens, where the nickel-copper specimens of approximately the same composition appeared to be somewhat better than the other specimens. It should be noted that the scale on the 9-year nickel-copper steel specimens was removed, whereas, the 4-year specimens were coated with a hard, uniform layer of mill scale. The acceleration of pitting resulting from local failure of the oxide coating would account for the relatively poor performance of the 4-year nickel-copper specimen (*B*) as compared with the 9-year specimen (*D*) of the same composition.

TABLE 19.—*Maximum penetration of alloy iron and steel plates exposed for 4 years*

[In mils]

No.	Soil Type	Open-hearth steel	Open-hearth iron		Low-alloy steel				4 to 6% chromium steel			High-alloy steel
			0.45% Cu 0.07% Mo	0.54% Cu 0.13% Mo	0.95% Cu 0.52% Ni	1.01% Cu 1.96% Ni	Cr-Si-Cu-P steel 1.02% Cr	2.01% Cr 0.57% Mo	5.02% Cr	4.67% Cr 0.51% Mo 0.030% Al 0.022% Ti	5.76% Cr 0.43% Mo 0.027% Ti	18% Cr
		A	*O*	*N*	*J*	*B*	*C*	*KK*		*E*	*H*	H_1
53	Cecil clay loam	76	74	[a] 72	57	56	64	52	57	50	57	----------
55	Hagerstown loam	54	44	51	50	52	51	52	48	47	39	----------
56	Lake Charles clay	[b] 100	116	100	96	[b] 139	[b] 77	[b] 60	95	[b] 80	[b] 90	----------
58	Muck	[b] 61	[b] 48	44	[b] 64	[b] 52	[b] 52	[b] 42	[b] [i] 44	[b] 46	[b] [e] 44	[e] 42
60	Rifle peat	40	28	[a] 26	[b] 40	28	[b] 67	[b] 26	[b] 51	36	32	----------
61	Sharkey clay	[b] 50	66	54	63	[i] 56	41	35	36	36	32	----------
62	Susquehanna clay	47	38	49	60	69	44	56	52	46	58	----------
63	Tidal marsh	[e] 26	[a] 48	47	28	25	41	24	70	73	72	----------
64	Docas clay	78	75	76	84	88	70	70	60	[b] 66	72	----------
65	Chino silt loam	51	65	[a] 57	60	[a] 84	44	[i] 55	46	48	56	----------
66	Mohave fine gravelly loam	[c] [d] 188+	84	[i] 98	[i] 85	73	[b] 80	130+	[b] 99	88	117	----------
67	Cinders	[a] [b] [e] 132+	[e] [f] [g] 55	[b] [e] 74	[b] [f] [g] 90	[b] [f] [g] 84	[b] 47	[b] [e] 68	[b] 57	[b] [e] 52	[b] [f] [g] 44	----------
69	Houghton muck	22	20	16	15	12	42	27	39	26	33	----------
70	Merced silt loam	[b] 77	[a] 97	[e] 122	82	78	[b] 94	[i] 94	121	[b] [b] 106	94	----------

[a] Data for the individual specimens differed from each other by more than 50%.
[b] No original surface; impossible to measure true penetration.
[c] Data on 1 specimen only.
[d] + mark in all cases indicates 1 or more specimens punctured.
[e] Severe corrosion at 1 end.
[f] Plate entirely destroyed at 1 end.
[g] Data for 1 specimen—impossible to obtain data from other specimen because of loss of original surface caused by corrosion.
[h] Hole from both sides.
[i] Average pit depths of the 1939 removals are greater.

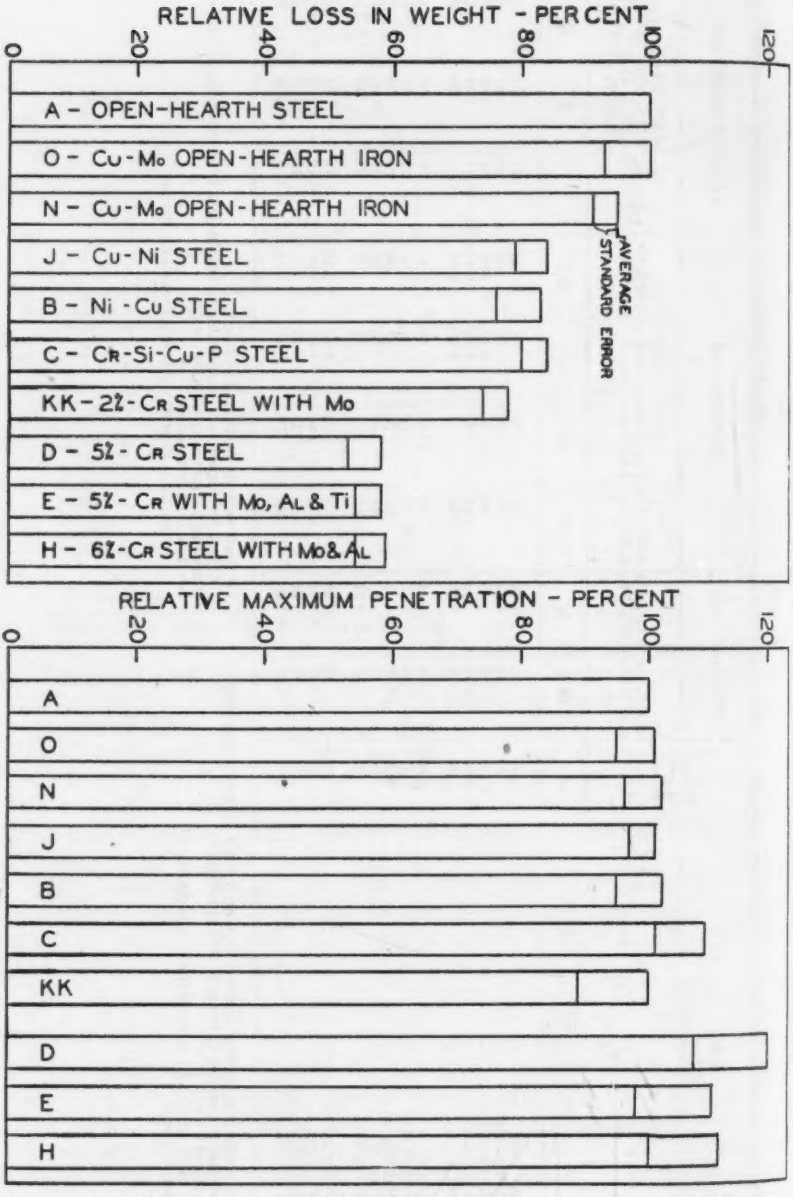

FIGURE 6.—*Relative loss of weight and maximum penetration of wrought ferrous materials for two periods of exposure.*

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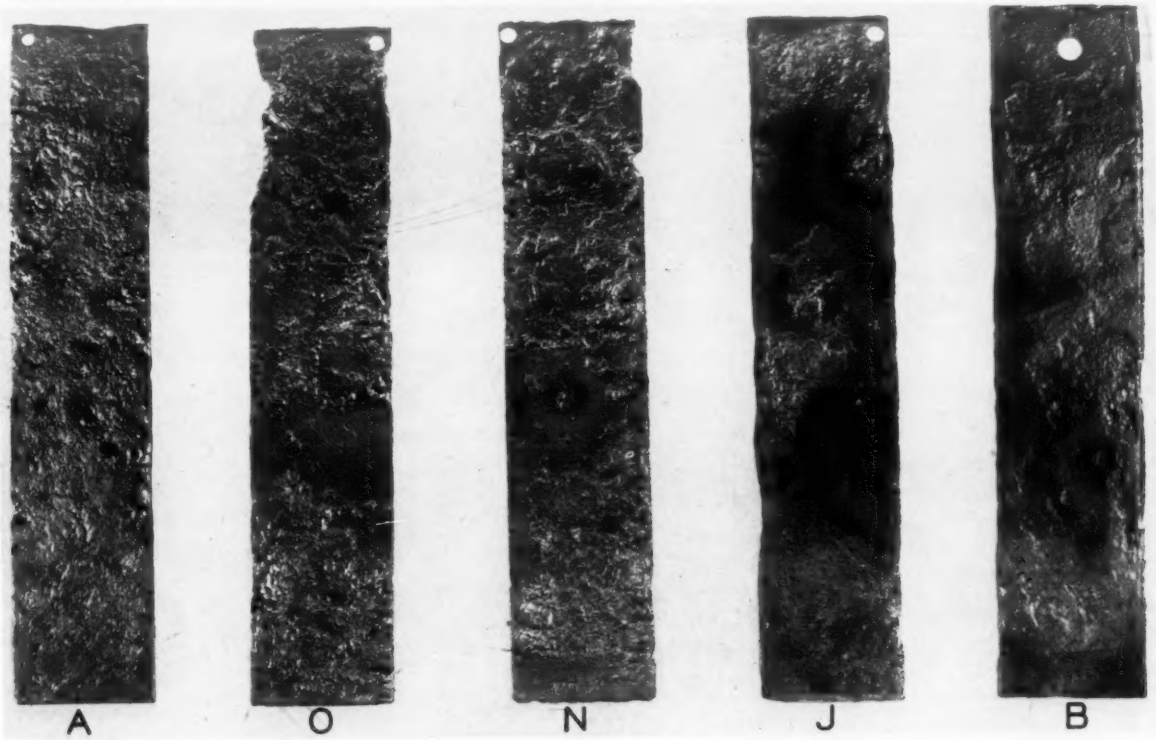

FIGURE 7.—*Ferrous plates exposed 4 years to Merced silt loam at Buttonwillow, Calif.*

See table 10 for the composition of the specimens.

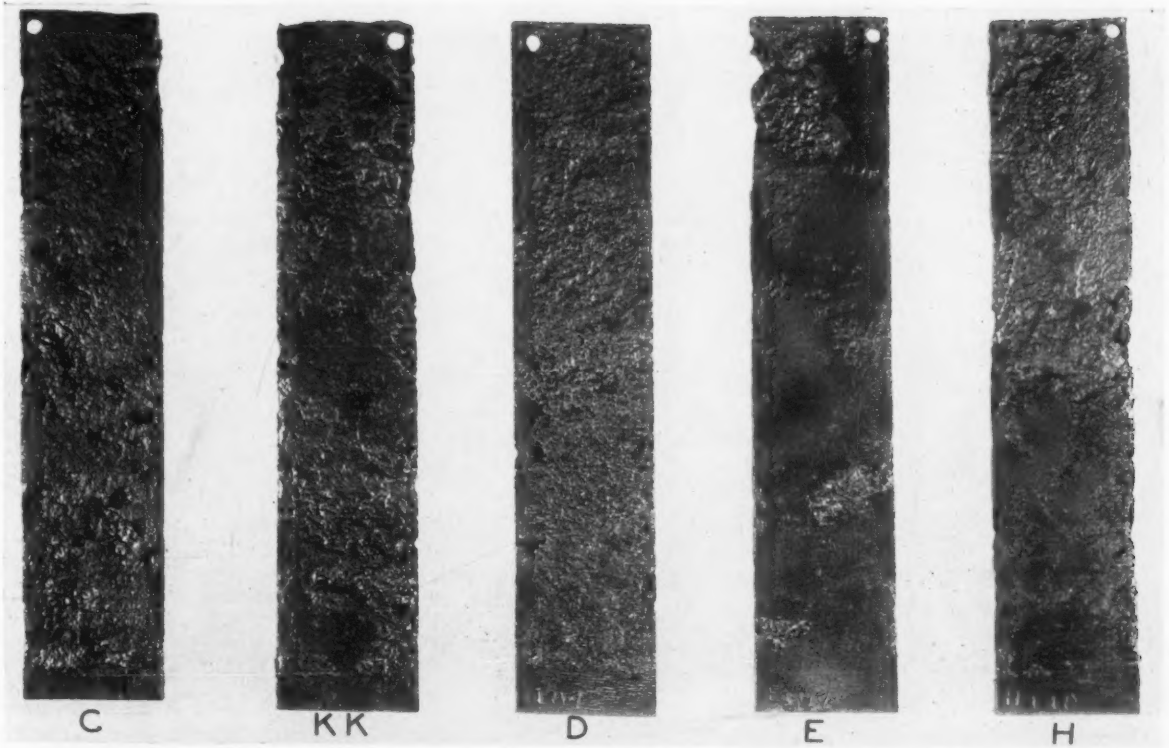

FIGURE 8.—*Ferrous plates exposed 4 years to Merced silt loam at Buttonwillow, Calif.*
See table 10 for the composition of the specimens.

TABLE 20.—*Relative loss of weight and maximum penetration of alloy iron and steel plates*

[Average of two periods of exposure, in percent]

Identification	Material	Loss of weight			Maximum penetration		
		Average	Standard deviation	Standard error	Average	Standard deviation	Standard error
A	Open-hearth steel	100			100		
O	Open-hearth iron (.48% Cu; .07% Mo)	100	38	7	101	31	6
N	Open-hearth iron (.54% Cu; .13% Mo)	95	19	4	102	35	6
J	Low-alloy (.95% Cu; .52% Ni)	84	25	5	101	24	4
B	Low-alloy (1.01% Cu; 1.96% Ni)	83	36	7	102	36	7
C	Low-alloy (Cr-Si-Cu-P steel; 1.02% Cr)	84	19	4	109	45	8
KK	Low-alloy (2.01% Cr; .57% Mo)	78	20	4	100	58	11
D	4 to 6% Cr steel (5.02% Cr)	58	27	5	120	70	13
E	4 to 6% Cr steel (4.67% Cr; .51% Mo; .030% Al; .022% Ti).	58	24	4	110	66	12
H	4 to 6% Cr steel (5.76% Cr; .43% Mo; .027% Al.).	59	26	5	111	61	11

It is, of course, possible for a material to be much more resistant to corrosion under some soil conditions than to others. For this reason table 20 is not useful for the selection of a material for a specific soil condition. Probably more definite conclusions can be drawn after the remainder of the specimens have been examined.

Figures 7 and 8 show the low-alloy plates exposed to soil 70. Areas where the mill scale was left intact on the nickel-copper (*B*) and copper-nickel (*J*) steels are clearly shown.

(d) SPECIMENS EXPOSED FOR 2 YEARS

Table 21 shows the averages of the losses of weight and maximum penetrations for two low alloys and the two high alloys buried in 1939. The plates containing 20 percent of chromium and 22 percent of nickel had a peculiar roughening of the surface over large areas when buried, especially near the ends of the specimens, which had the appearance of true pitting. None of these pits measured greater than 6 mils. Therefore, unless definite pits deeper than 6 mils are observed on these plates in future removals, the plates will be classified as unaffected.

Although the losses of weight and depths of maximum penetration of the two high-alloy materials in table 21 are slight, there is a consistent difference favoring the higher alloy. It is too soon to reach definite conclusions as to the relative merits of the copper-molybdenum steel and the chromium-molybdenum steel. The reader is cautioned against comparing these data with data for other materials exposed for the same length of time but buried at an earlier or later date, since two periods equal in length may differ considerably in amount or distribution of rainfall. For longer periods of exposure these differences will be of less importance.

TABLE 21.—*Loss of weight and depth of maximum penetration of low-alloy and high-alloy steel specimens exposed for 2 years*

U, apparently unaffected by corrosion.
M, shallow metal attack, roughening of the surface but no definite pitting.
P, definite pitting but no pits on either specimen greater than 6 mils.

Soil		Exposure	.05% Cu, .07% Mo open-hearth iron (plate)		2% Cr steel with .49% Mo (pipe)		20% Cr, 22% Ni steel (plate)		18% Cr, 11% Ni steel (plate)	
			MM		*NN*		*DT*		*CM*	
No.	Type		Loss of weight	Maximum penetration	Loss of weight	Maximum penetration	Loss of weight	Maximum penetration	Loss of weight	Maximum penetration
		Years	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*	*oz/ft²*	*Mils*
53	Cecil clay loam	1.91	[a] 2.32	[a] 42	1.97	65	0.0048	*U*	0.0054	*M*
55	Hagerstown loam	2.03	0.92	44	0.92	59	.0065	*U*	.0061	*M*
56	Lake Charles clay	1.91	11.16	60	13.81	78	.0033	*U*	.0067	*M*
58	Muck	1.91	4.70	48	5.88	46	.0017	*U*	.0053	*P*
60	Rifle peat	1.91	3.44	16	4.08	18	.0017	*U*	.0038	*P*
61	Sharkey clay	1.92	2.32	41	1.98	42	.0032	*U*	.0063	*U*
62	Susquehanna clay	1.90	2.96	40	2.57	40	.0020	*U*	.0074	*P*
63	Tidal marsh	1.88	2.08	22	1.76	38	.0046	*U*	[b] .0084	[b] *M*
64	Docas clay	1.90	4.09	47	3.92	40	.0018	*U*	.0063	*M*
65	Chino silt loam	1.91	[a] 3.14	[a] 43	3.87	51	.0048	*U*	.0067	*M*
66	Mohave fine gravelly loam	1.86	6.64	71	9.02	[c] 145+	.0041	*U*	.0095	*P*
67	Cinders	1.90	25.97	128	17.75	124+	.0042	*U*	.0056	*U*
69	Houghton muck	1.90	[a] 2.25	[a] 13	1.89	22	.0018	*U*	.0060	*U*
70	Merced silt loam	1.90	10.07	92	12.81	130+	.0035	*U*	.0078	*M*

[a] Data for 1 specimen only.
[b] Data for 3 specimens.
[c] + Indicates that 1 or both specimens contained holes due to corrosion.

IV. COPPER AND COPPER-ALLOY

1. DIMENSIONS AND COMPOSITION

Table 22 shows the dimensions and composition of the copper and copper-alloy specimens. It will be noted that the principal alloying elements are zinc, tin, silicon, and nickel. With one exception, the specimens are sections of pipe, the ends of which were closed.

TABLE 22.—*Dimensions and composition of copper and copper-alloy specimens*

Material	Identification	Year buried	Form	Width or diameter	Length	Wall thickness
				in.	*in.*	*in.*
Tough-pitch copper	*C*	1932	Pipe	1.7	12	0.145
Deoxidized copper	*A*	1932	do	1.7	13	.144
Copper with soldered fittings	*M*	1932	do	1.5	12	.062
Red brass	*F*	1932	do	1.7	12	.143
Admiralty metal	*H*	1932	do	1.7	12	.143
Two-and-one-leaded brass	*K*	1932	do	1.7	12	.08
Brass	*J*	1932	do	1.7	13	.145
Muntz metal	*L*	1932	do	1.7	12	.08
Muntz metal with arsenic	B_1	1939	Plate	2.5	12	.25
Bronze	*E*	1932	Pipe	1.7	12	.141
Copper-silicon alloy	*N*	1932	do	1.7	12	.145
Do	*D*	1932	do	1.7	12	.143
Copper-nickel alloy	*G*	1932	do	1.7	12	.145

Material	Cu	Zn	Sn	Pb	Ni	Fe	Si	Mn	P	As
	%	%	%	%	%	%	%	%	%	%
Tough-pitch copper	99.9								0.0	
Deoxidized copper	99.94								.018	
Copper with soldered fittings										
Red brass	85.18	14.80				0.01				
Admiralty metal	71.28	27.39	1.30	0.01		.02				
Two-and-one-leaded brass	67.08	31.07		.84		Trace	1.01			
Brass	66.50	33.06		.42		0.02				
Muntz metal	60.06	39.58		.36		Trace				
Muntz metal with arsenic	62.37	37.54		.005		0.007				0.08
Bronze	97.15		1.80			.01	1.04			
Copper-silicon alloy	98.11		0.14		.01	.11	1.49	0.18		
Do	95.46				.08	.21	3.19	1.06		
Copper-nickel alloy	74.45	4.99			20.04			0.52		

2. SPECIMENS EXPOSED FOR 9 YEARS

Table 23 shows the losses of weight of the copper and copper-alloy specimens exposed for 9 years. As a basis for comparison, the losses of open-hearth-steel specimens in the same soils have been added. It will be noted that in most cases the losses of weight of the copper and copper-alloy specimens were less than 10 percent of that of the steel. Table 24 shows the condition of the copper and copper-alloy specimens with respect to pitting. The corrosion of these specimens is much more uniform than that of steel, and the maximum pit depths are much less. Apparently these statements do not apply to the specimens in Rifle peat, soil 60. This is a very acid organic soil. For some reason open-hearth steel does not pit badly in this soil, although it loses considerable weight. In considering the relative merits of ferrous and nonferrous pipe, it should be remembered that some of the nonferrous pipe is frequently made with thinner wall thickness than is standard for steel pipe of the same diameter, although some materials, such as red brass, are always furnished in standard steel pipe thickness.

TABLE 23.—*Loss of weight of copper and copper alloys exposed for 9 years*

[In ounces per square foot]

No.	Soil Type	Exposure	Tough pitch copper	Deoxidized copper	Red brass	Admiralty metal	2-and-1-leaded brass	Brass 66% Cu 33% Zn	Muntz metal	Bronze 97% Cu 1% Si 1.8% Sn	Alloy 98% Cu 1.5% Si 0.2% Mn	Alloy 98% Cu 1.5% Si 0.2% Mn	Alloy 95% Cu 3% Si 1% Mn	Alloy 75% Cu 20% Ni 5% Zn	Low-carbon steel
			C	*A*	*F*	*H*	*K*	*J*	*L*	*E*	*N*	[a] N_1	*D*	*G*	*N*
		Years													
53	Cecil clay loam	9.47	0.24	0.22	0.25	0.29	0.47	[b] 0.41	0.52	0.37	0.30	----------	0.36	0.27	4.09
55	Hagerstown loam	9.11	.20	.18	.25	.25	.36	.30	.77	.35	.30	----------	.28	.20	3.82
56	Lake Charles clay	9.42	.71	.78	.70	.57	.89	.94	1.21	.76	.62	----------	.63	.78	28.76
58	Muck	9.51	1.95	2.10	2.06	2.09	[b] 1.66	3.33	5.25	2.11	1.97	----------	2.12	1.40	16.24
59	Carlisle muck	9.12	0.12	0.11	0.12	[c] 0.086	0.20	0.029	0.031	0.17	[d] 0.24	----------	0.15	0.088	4.70
60	Rifle peat	9.24	7.26	5.01	3.55	[d] 2.85	[d] 3.22	[d] 4.21	[d] 4.56	[d] 3.22	[d] 3.96	1.82	4.46	3.61	16.72
61	Sharkey clay	9.53	0.33	0.35	0.41	0.51	0.87	[i] 1.22	[i] 2.58	0.61	0.48	----------	0.52	0.43	5.78
62	Susquehanna clay	9.47	.36	.48	.43	.53	.71	0.94	1.79	.69	.57	----------	.60	.47	6.65
63	Tidal marsh	9.55	4.46	[i] 4.22	[i] .75	.18	[d] .52	.076	0.10	[d] 4.38	6.96	----------	5.32	3.56	9.03
64	Docas clay	9.21	2.80	5.32	[d] 1.12	.98	[d] 1.07	[i] 1.94	11.53	2.30	4.87	----------	2.88	[d] 0.74	[e] *D*
65	Chino silt loam	9.25	0.26	[i] 0.24	0.28	.58	1.39	[i] 1.60	[i] 1.45	[i] 0.96	[i] 0.62	----------	[i] 0.48	.44	12.86
66	Mohave fine gravelly loam	9.23	.45	[di] .62	.77	.80	[i] 0.95	[d] 1.16	[i] 1.41	[d] 1.53	[d] .51	0.34	.55	[d] .60	18.56
67	Cinders	9.24	9.84	11.50	8.46	8.27	([f]*Z*)	[e][i] 23.10	([f]*Z*)	8.76	22.51	23.17	13.47	6.28	[h] 58.39

[a] These specimens had brazed joints; date for 1 specimen only.
[b] Data for 1 specimen only.
[c] Average for 3 specimens.
[d] Data for the individual specimens differ from each other by more than 50%.
[e] *D* indicates specimens destroyed by corrosion.
[f] *Z* indicates specimens destroyed by dezincification.
[g] Data for 1 specimen; the other specimen was destroyed by dezincification.
[h] Data for 1 specimen; the other specimen was destroyed by corrosion.
[i] Average loss of weight for 1939 removals is greater.

TABLE 24.—*Maximum penetration of copper and copper alloys exposed for 9 years*

TABLE 24.—*Maximum penetration of copper and copper alloys exposed for 9 years*

[In mils]

M, shallow metal attack, roughening of the surface but no definite pitting.
P, definite pitting, no pits greater than 6 mils.
s, uniform corrosion, impossible to measure true penetration.
D, selective corrosion, such as dezincification over large areas.
d, selective corrosion over small areas.
Z, specimens destroyed by corrosion (dezincification).
+, one or both specimens punctured.

Soil No.	Tough-pitch copper	Deoxidized copper	Copper with soldered joints	Red brass	Admiralty brass	Two- and-one-leaded brass	Brass 66% Cu 33% Zn	Muntz metal	Bronze 97% Cu 1% Si 1.8% Sn	Alloy				Low-carbon steel
										98% Cu 1.5% Si 0.2% Mn	98% Cu 1.5% Si 0.2% Mn	95% Cu 3% Si 1% Mn	75% Cu 20% Ni 5% Zn	
	C	*A*	[a] *M*	*F*	*H*	*K*	*J*	*L*	*E*	*N*	[b] *N*	*D*	*G*	*N*
53	6	*P*	13	10, *D*	20, *D*	P, *D*	6, *D*	6, *D*	12	*P*	----------	8	8, *D*	59
55	8	*P*	8	7, *D*	20, *D*	7, *D*	10, *D*	6, *D*	[c] 20	*P*	----------	8	6, *D*	59
56	*P*	*P*	[d] 15	*P*, *D*	*P*, *D*	*P*, *D*	P, *D*	*P*, *D*	12	*P*	----------	*M*	*P*, *D*	[e] 154+(7)
58	10	[e] 14	18	10, *D*	[f] 26, *D*	[g] *P*, *D*	8, *D*	6, *D*	53	12, *s*	----------	12, *s*	*P*, *D*	110, *s*
59	6	*P*	9	*M*	[d] *P*	*P*	*M*, *D*	*P*, *D*	20	*M*	----------	*P*	*P*	[e] 40
60	40, *s*	38, *s*	[e] 17, *s*	34, *D*	[c] 16, *s*, *d*	[e] 12, *D*	[e] 33, *D*	[e] 27, *s*, *D*	18, *s*	10, *s*	8	21, *s*	32, *D*	[e] 27, *s*
61	8	8	10	[f] 7, *D*	[c] 35, *D*	6, *D*	6, *D*	[f] 12, *D*	[e] 37	10	----------	*P*	[f] *P*, *D*	[e] 96
62	8	8	10	14, *D*	[f] 24, *D*	*P*, *D*	13, *D*	*P*, *D*	22	*P*	----------	6	12, *D*	[e] 87
63	6	10, *s*	6, *s*	6	*P*, *d*	*P*	*M*, *D*	*P*, *d*	10, *s*	12, *s*	----------	9	*P*	54
64	[e] 14	[e] 16	[e] 13	26, *d*	[e] 46, *D*	[e] 15, *D*	[f] 20, *D*	[e] [h] 42+, *D*	34	21, *s*	----------	[e] 16	[e] 18, *D*	154+(5, 7)
65	[f] 10	*P*	[f] 8	*P*, *D*	[f] 13, *D*	*P*, *D*	[e] [f] 18, *D*	*P*, *D*	[f] 22	20	----------	11	*P*, *D*	112
66	*P*	10	[f] 13	*P*, *D*	[f] *P*, *D*	*P*, *D*	8, *D*	*P*, *D*	22	13	*P*	9	*P*, *D*	154+(5, 7)
67	51, *s*	58, *s*	145+(5)	[e] 54, *D*	68, *s*, *D*	*Z*(5, 7)	[i] 132+(2, 5, 7)	*Z*(2, 5, 7)	102	145+	90, *s*	80, *s*	36, *D*	154+(2, 5, 7)

[a] These specimens had streamlined caps and couplings soldered in place.
[b] These specimens had brazed joints; data for only 1 specimen.
[c] Maximum pits for individual specimens differed from each other by more than 50 percent.
[d] Data for 3 specimens.
[e] A number in parentheses after the pit depth indicates that 1 or both specimens of a previous removal was punctured, e. g., (5) indicates that the specimen was punctured after 5 years.
[f] Average pit depths of 1939 removals are greater.
[g] Data for 1 specimen only.
[h] Hole in 1 specimen due to dezincification. The mate, although it had no measurable pits greater than 8 mils, was badly dezincified, as indicated by the flat sound when the pipe was struck with another piece of metal.
[i] 1 specimen destroyed by dezincification.

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To facilitate the comparison of materials and minimize the effects of abnormalities in the performance of individual specimens, table 25 has been prepared. In this table the losses of each material for the four periods of exposure have been expressed on a relative percentage basis in terms of the loss of tough pitch copper *C*, which was given the value of 100 percent. The data from soils 63 and 67 were omitted in these averages, the former because the loss of weight of the specimens followed a different trend from that shown by the other soils, the latter because of the complete destruction of the brasses.

TABLE 25.—*Relative loss of weight of copper and copper alloys*

[Average of four periods of exposure]

Material		Composition			Average	Standard deviation	Standard error
Symbol	Type	Cu	Zn	Pb			
		%	%	%	%	%	%
C	Tough-pitch copper	99.9			100		
A	Deoxidized copper	99.94			144	93	12
F	Red brass	85.2	14.8		105	32	5
H	Admiralty metal	71.3	27.4		121	53	8
K	Two-and-one leaded brass	67.1	31.1	0.8	176	176	25
J	Brass	66.5	33.1	.4	225	229	33
L	Muntz metal	60.1	39.6	.4	492	942	136
		Cu	Si	Sn			
E	Bronze	97.2	1.0	1.8	193	144	21
N	Copper-silicon alloy	98.1	1.0		154	79	11
D	do	95.5	3.2		142	63	9
		Cu	Zn	Ni			
	Copper-nickel alloy	74.5	5.0	20.0	104	54	8

The corrosion losses shown in table 25 in general increase with the increase in zinc content. This is in agreement with statements made previously [2, 3], that brasses containing high percentages of zinc are in general much less resistant to corrosion in soils than copper or high-copper alloys. However, a similar table for the specimens exposed to Tidal marsh, soil 63, would show the reverse. A probable explanation for this difference is the greater resistance of low-copper brasses to sulfides. The relative loss of weight of the deoxidized copper (*A*) is not in agreement with the other specimens in table 25, but this may be a result of a mechanical effect, since it is believed that some of these specimens may have been injured in rolling.

In some soils the losses of the brasses do not indicate the extent of corrosion, since part of the zinc was removed by selective corrosion, which weakened the material. Nor do the pit depths for some brasses indicate the extent of corrosion in soils in which dezincification occurred, since the maximum depth of dezincification was not determined except where the specimens were cracked.

It previously has been suggested [2] that because of the degree of consistency shown in a tabulation similar to table 25 for the three periods of exposure, the relative order indicated might be accepted tentatively as the order of merit of the materials for soil conditions

generally. However, as loss of weight is only one criterion of behavior; consideration would also have to be given to the depth of pitting and the tendency of the material to dezincify. Hence, the order of merit of the brasses shown in table 25 does not show the true comparative worth of the materials because the loss in weight or depth of pitting due to dezincification has not been taken into account. This will be made clearer in the discussion to follow, involving a more detailed examination of some of the brass specimens.

In table 24, selective corrosion, such as dezincification, was reported on most of the brass specimens. The type of corrosion was determined by visual inspection of the specimens before cleaning, which revealed copper-colored spots over large portions of the exposed surface in the attacked areas. Contrary to expectations, selective corrosion was also observed on red brass (*F*) and the copper-nickel-zinc alloy (*G*). No differences were evident between the type of corrosion on the brasses in which dezincification is normally expected and that on specimens *F* and *G*. In order to determine whether any real selective corrosion, such as dezincification, had taken place, a transverse section was cut from a region which showed the copper-colored spots on one of each of the brass and copper-nickel-zinc alloy specimens which were exposed to Sharkey clay, soil 61. These sections were subjected to a microscopic examination through the courtesy of H. L. Burghoff, research metallurgist of the Chase Brass & Copper Co. A brief description of the appearance of each of the materials by Mr. Burghoff and his discussion follow:

"Yellow brass pipe (*J*)—66.50% Cu, 0.42% Pb, 0.02% Fe, 33.06% Zn.—Definite areas of dezincification are visible on the outer surface. A section through one of the most pronounced of these areas shows that dezincification has progressed to about 40 percent of the wall thickness of the pipe. See figure 9.

"Two-and-one leaded brass tube (*K*)—67.08% Cu, 0.84% Pb, 1.01% Si, 31.07% Zn.—Dezincification is visible on the outer surface of this specimen. A section through the dezincified region shows that the tube wall has been completely penetrated by the dezincification attack. The microstructure is similar to that of Muntz metal and dezincification begins in the "beta" phase. Corrosion of this material, which is not a commercial pipe material, is more severe than that of specimen *J*. See figures 10, A and B.

"Muntz metal tube (*L*)—60.06% Cu, 0.36% Pb, 39.58% Zn.—This specimen has suffered uniform or layer type dezincification over the entire surface. The tube has been corroded considerably, but the dezincified layer is very thin. See figures 11, A and B.

"Admiralty metal (*H*)—71.28% Cu, 1.30% Sn, 0.01% Pb, 0.02% Fe, 27.39% Zn.—Some dezincification of this specimen is evident, but its extent is so slight that it can be called superficial. See figure 12.

"Red Brass (*F*)—85.18% Cu, 0.01% Fe, 14.80% Zn.—Some fine red spots are visible on the roughened surface of this specimen. Microscopic examination shows these to be dezincification, but the extent of this is so slight as to be merely superficial. See figures 13, A and B.

"Copper-nickel-zinc alloy (*G*)—74.45% Cu, 20.04% Ni, 4.99% Zn, 0.52% Mn.—Some reddish discoloration is apparent upon the surface. Microscopic examination shows this to be the result of a very super-

ficial selective attack that must involve loss of both nickel and zinc in order to give the resulting copper. See figure 14.

"It is possible to place the materials into three groups according to the nature of the attack. Red brass (*F*), copper-nickel-zinc alloy (*G*), and Admiralty metal (*H*), showing superficial selective corrosion, would be in the first group. Yellow brass (*J*) and the so-called two-and-one leaded brass (*K*), which is actually a leaded silicon brass, showing definite and deeply penetrating local dezincification, would be in the second group. Muntz metal (*L*), which suffered the uniform or layer type dezincification, would be in the third group.

"The materials *K* and *J* differ in composition somewhat, there being 0.84 percent of lead and about 1 percent of silicon in the *K* and only 0.42 percent of lead and no silicon in the *J*. There is a very marked difference in the structure of the two alloys. In specimen *J* there are grains of the alpha phase and particles of lead, the structure being entirely characteristic for yellow-brass pipe. In the *K* specimen, on the other hand, there are grains of the alpha phase, a "beta" phase, and lead. The occurrence of the "beta" is a result of the presence of silicon. This structure is analogous to that of Muntz metal. Both the materials *K* and *J* have suffered dezincification in the soil-corrosion tests. On the basis of the weight loss and depth of pitting shown in tables 23 and 24, and disregarding the dezincification, *K* may be considered to be somewhat superior to *J* in soil 61. The fallacy of this judgment is shown by a study of the photomicrographs of corroded areas of the two materials in figures 10 to 14. Although exact comparison of the depth of dezincification in the pipe is not possible because of differences in wall thickness of the specimens, it is evident that the yellow brass is superior to the two-and-one leaded brass. Dezincification has completely penetrated the wall of the *K* specimen over a considerable area, and it is not possible to determine how deeply it would have penetrated if the wall had been heavier. On the other hand, dezincification in the *J* specimen has penetrated the heavy wall of this pipe by an amount which is definitely less than the wall thickness of the *K* specimen. The difference in the behavior of the two materials should be ascribed entirely to the silicon present in the leaded silicon brass tube (*K*) and not to the difference in the amounts of the unimportant (corrosion-wise) lead."

It should be noted that the extent of the corrosion of the red brass, Admiralty and Muntz metals, and the copper-nickel-zinc alloy on the specimens exposed to soil 61 is adequately defined by the observed weight losses and depth of pitting in tables 23 and 24. On the other hand, the dezincification attack on the yellow brass and on the two-and-one leaded brass is of such extent that it can only be properly evaluated by sectioning the test pieces. Weight losses and depth of pitting have almost no significance in these two cases. These conclusions have been based on the examination of one of each of the brass specimens exposed to Sharkey clay. Since it has previously been shown that soil-corrosion data are sometimes inconsistent, the relationship shown by single specimens in the one soil may not hold in the other soils. Hence, the measurement of the depth of dezincification for all the brasses where this type of attack occurred would unquestionably be highly desirable. This work can not be undertaken at the National Bureau of Standards at present. However, the specimens will be preserved and an attempt will be made to make these measure-

FIGURE 9.—*Yellow brass exposed 9.53 years to Sharkey clay.*
Transverse section showing uncorroded metal (below) and dezincified metal (above). ×500.

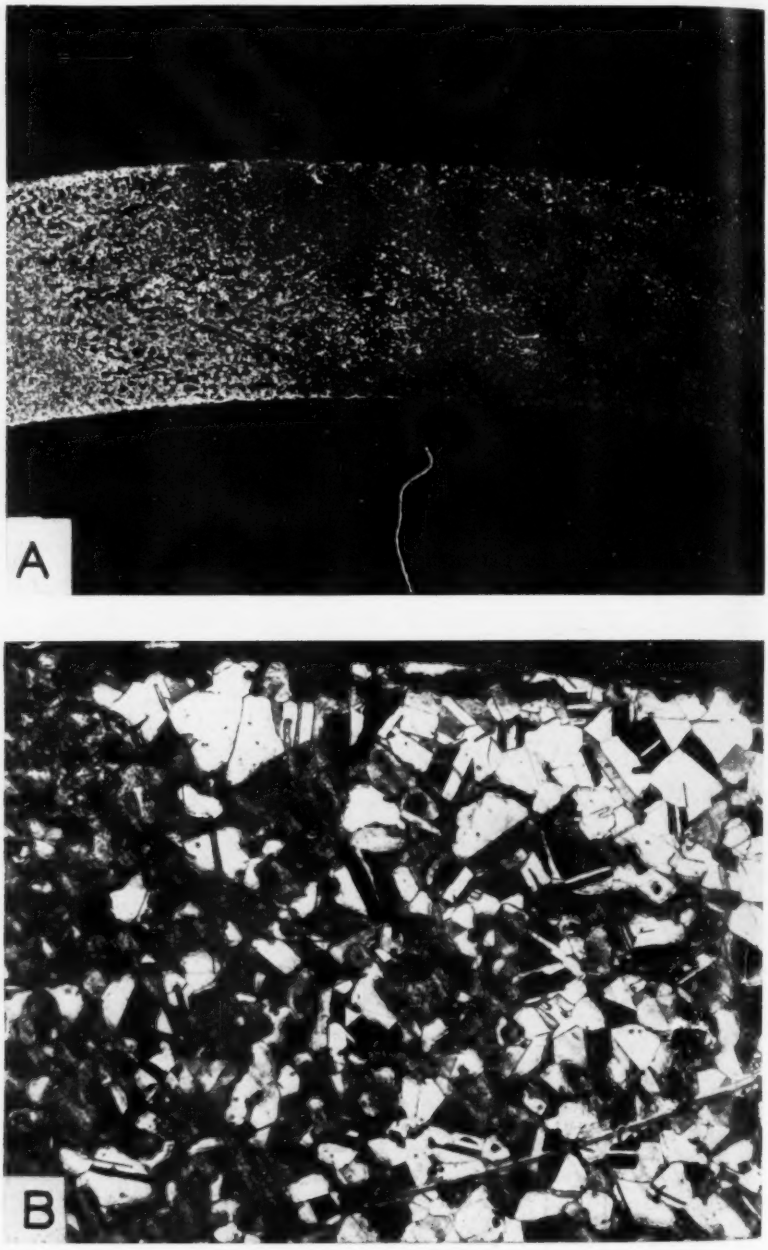

FIGURE 10.—*Two-and-one leaded brass (leaded silicon brass) exposed 9.53 years to Sharkey clay.*

A, Transverse section showing transition from uncorroded metal at left to complete dezincification at right. ×15; *B*, section showing partial dezincification, the dezincification being more severe at the left. ×250.

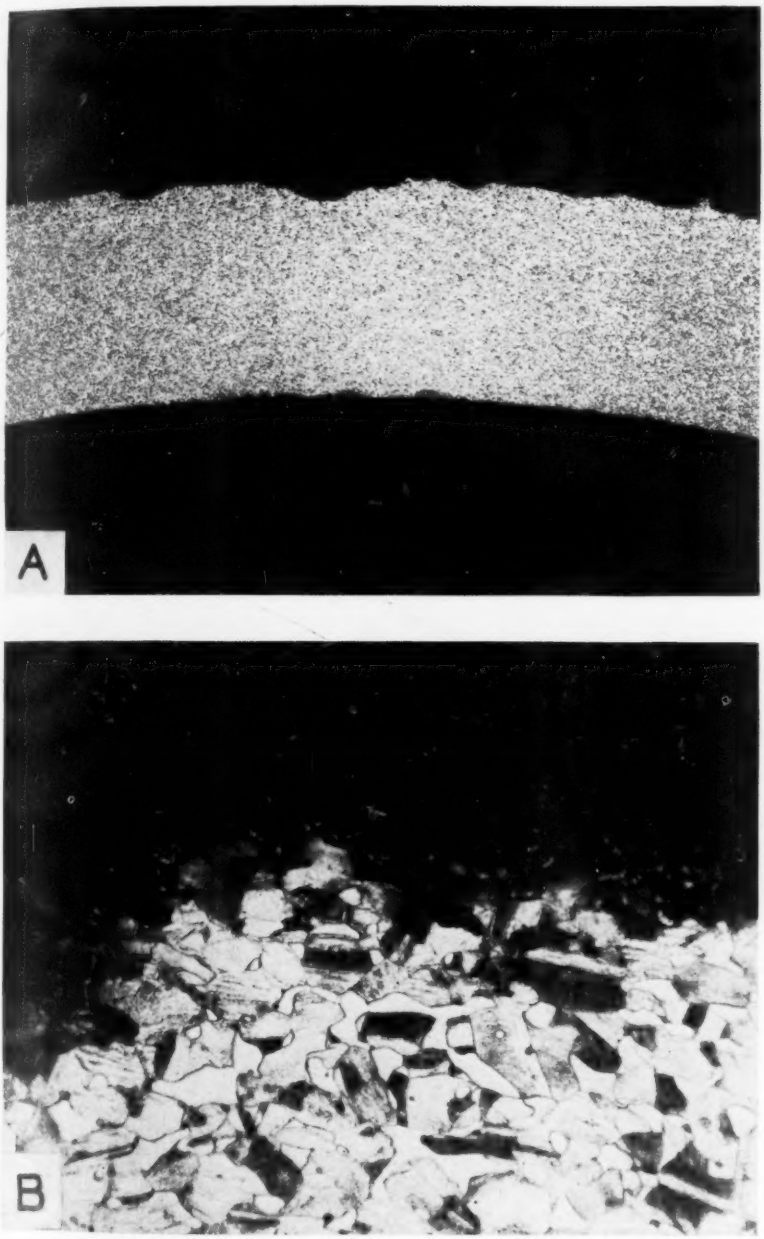

FIGURE 11.—*Muntz metal exposed 9.53 years to Sharkey clay.*

A, Transverse section showing outer surface roughened by corrosion. The uniformly dezincified layer, which is about 5 percent as thick as the uncorroded metal, is not evident in this photograph. ×15. *B*, dezincified mass evident in upper portion. ×500.

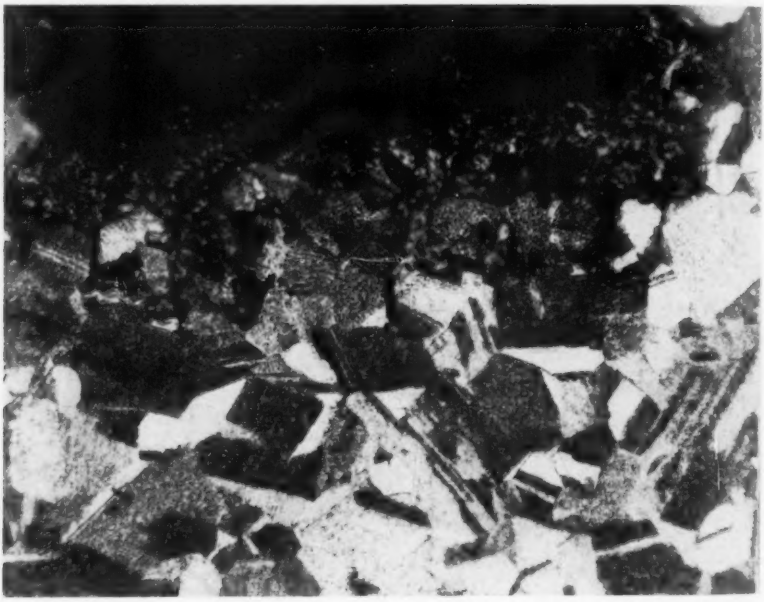

FIGURE 12.—*Admiralty metal exposed 9.53 years to Sharkey clay.*
Transverse section to show thin layer dezincified metal. ×500.

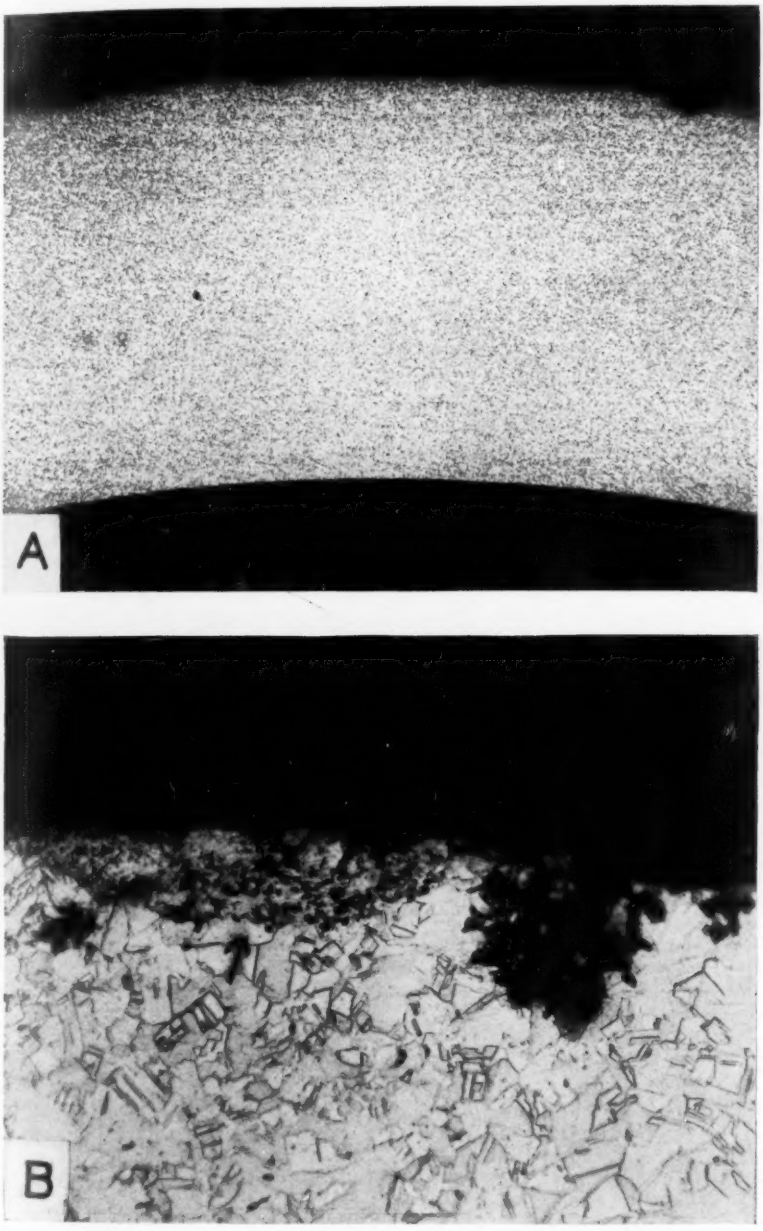

FIGURE 13.—*Red brass exposed 9.53 years to Sharkey clay.*

A, Transverse section showing outer surface roughened by corrosion. ×15; *B*, section through pipe wall to the insignificant and superficial character of one dezincified spot included in the area covered by *A*. ×500.

FIGURE 14.—*Copper-nickel-zinc-alloy exposed 9.53 years to Sharkey clay.*
Transverse section showing small mass of copper, a result of very slight selective attack. ×500.

ments at a more convenient time in the future. Until such measurements are made, the order of merit of the brasses shown in table 25 should not be taken as indicative of their comparative worth.

3. MUNTZ METAL SPECIMENS EXPOSED FOR 2 YEARS

The copper alloy containing approximately 60 percent of copper and 40 percent of zinc, commonly known as Muntz metal, is subject to dezincification under several soil conditions. To determine whether the addition of arsenic to this alloy would prevent dezincification, specimens of Muntz metal plates containing 0.08 percent of arsenic were added to the tests in 1939. Unfortunately, similar plates of ordinary Muntz metal were not buried at the same time. This makes it necessary to compare the behavior of the new materials with that of a section of pipe buried 7 years previously. Obviously, under these conditions small difference in performance may be accidental. Table 26 shows the losses of weight and conditions of the two materials exposed for approximately the same periods. It appears that the addition of 0.08 percent of arsenic was insufficient to prevent dezincification of the brass. Greater resistance to dezincification for this type of material might have been observed if the alloy contained more arsenic. It is known that considerably more arsenic is required to inhibit dezincification in Muntz metal than in alpha brass [20].

TABLE 26.—*Loss of weight and maximum penetration of Muntz metal exposed 2 years*

M, shallow metal attack, roughening of the surface but no definite pitting.
P, definite pitting but no pits greater than 6 mils.
s, uniform corrosion, no reference surface.
D, selective corrosion by dezincification over large areas (several square inches per square foot).
d, selective corrosion over small areas.
Z, specimens destroyed by dezincification.

Soil		Arsenical Muntz metal (sheet) B_1			Muntz metal (pipe) *L*		
No.	Type	Exposure	Loss of weight	Maximum penetration	Exposure	Loss of weight	Maximum penetration
		Years	*oz/ft²*	*Mils*	*Years*	*oz/ft²*	*Mils*
53	Cecil clay loam	1.91	0.18	*P,D*	1.96	0.19	*P,d*
55	Hagerstown loam	2.03	.16	*P,d*	1.89	.19	6,*d*
56	Lake Charles clay	1.91	.55	12,*D*	1.99	.14	*M,d*
58	Muck	1.91	.54	*P,D*	1.99	.20	*P,d*
60	Rifle peat	1.91	1.87	13,*D*	1.92	1.73	9,*d*
61	Sharkey clay	1.92	.40	*P,D*	.95	.16	*P,d*
62	Susquehanna clay	1.90	.32	*P,D*	1.93	.33	*P,d*
63	Tidal marsh	1.88	[a].036	[a] *P*	2.04	1.41	M
64	Docas clay	1.90	.47	*P*	1.91	4.02	*P,D*
65	Chino silt loam	1.91	.21	*P,D*	1.91	2.43	*M,D*
66	Mohave fine gravelly loam	1.86	.30	8,*d*	1.92	[b].63	[b] *P,d*
67	Cinders	1.90	15.25	122,*sD*	2.02	*Z*	*Z*
69	Houghton muck	1.90	.30	*P,D*			
70	Merced silt loam	1.90	.28	12,*D*			

[a] Data for 3 specimens.
[b] Data for 1 specimen.

V. ZINC

Table 27 shows the dimensions and composition of two kinds of zinc specimens buried in 1937, and table 28 shows the losses of weight and maximum penetration of the specimens, which were exposed for approximately 4 years.

TABLE 27.—*Dimensions and composition of zinc specimens*

Material	Identification	Year buried	Form	Length	Width or diameter	Thickness of plate or coating	Al	Cu	Fe	Mg	Pb	Cd	Sn
				in.	*in.*	*in.*	%	%	%	%	%	%	%
Rolled zinc	Z	1937	Plate	12	2.3	0.15	.....	.....	0.009	.....	0.095	0.0038	.....
Die-casting zinc	CZ	1937	do	6.81	4.44	.125	4.00	1.05	.018	0.02 to 0.05	<.003	<.003	<0.001
Galvanized steel [a]	T	1937	Pipe	12	1.5	.00517	.008	.....	.07	.....	.78	.....	.....

[a] Analysis of spelter.

TABLE 28.—*Loss of weight and maximum penetration of zinc plates exposed for 4 years*

Soil		Rolled zinc Z		Die-cast zinc CZ	
No.	Type	Loss of weight	Maximum penetration	Loss of weight	Maximum penetration
		oz/ft²	*Mils*	*oz/ft²*	*Mils*
53	Cecil clay loam	0.62	10	0.54	22
55	Hagerstown loam	.60	[a] 8	.61	[a] 20
56	Lake Charles clay	3.42	[b] 26	4.96	30
58	Muck	5.09	66	6.33	[c] 125+(2)
60	Ride peat	10.36	[a] 100	14.98	125+
61	Sharkey clay	0.96	8	1.12	28
62	Susquehanna clay	1.24	9	0.60	16
63	Tidal marsh	[b] 2.30	34	1.43	24
64	Docas clay	0.57	18	2.53	20
65	Chino silt loam	.76	36	0.76	16
66	Mohave fine gravelly loam	[b] 2.61	[b] 28	4.74	124+
67	Cinders	[d] 12.16	[a] 118+(2)	13.08	125+
69	Houghton muck	1.70	10	1.64	36
70	Merced silt loam	[d] 1.62	[b] 102+	[d] 2.19	[b] 80+

[a] Uniform corrosion; no reference surface left.
[b] Data for individual specimens differed from the average by more than 50 percent.
[c] + Indicates that 1 or both specimens punctured by corrision from 1 side of the plate. (2) indicates that 1 specimen from the previous removal was punctured after 2 years.
[d] Data for 1 specimen only; the other specimen was destroyed by corrosion.

The data are in substantial agreement with similar data obtained after an exposure of 2 years and seem to indicate that with respect to loss of weight and to maximum penetration, the rolled-zinc specimens are superior to the die-cast zinc alloy. The rolled zinc specimens in the tidal marsh corroded more than the others during both periods of exposure. Figure 15 shows specimens of rolled and die-casting zinc exposed to three soils.

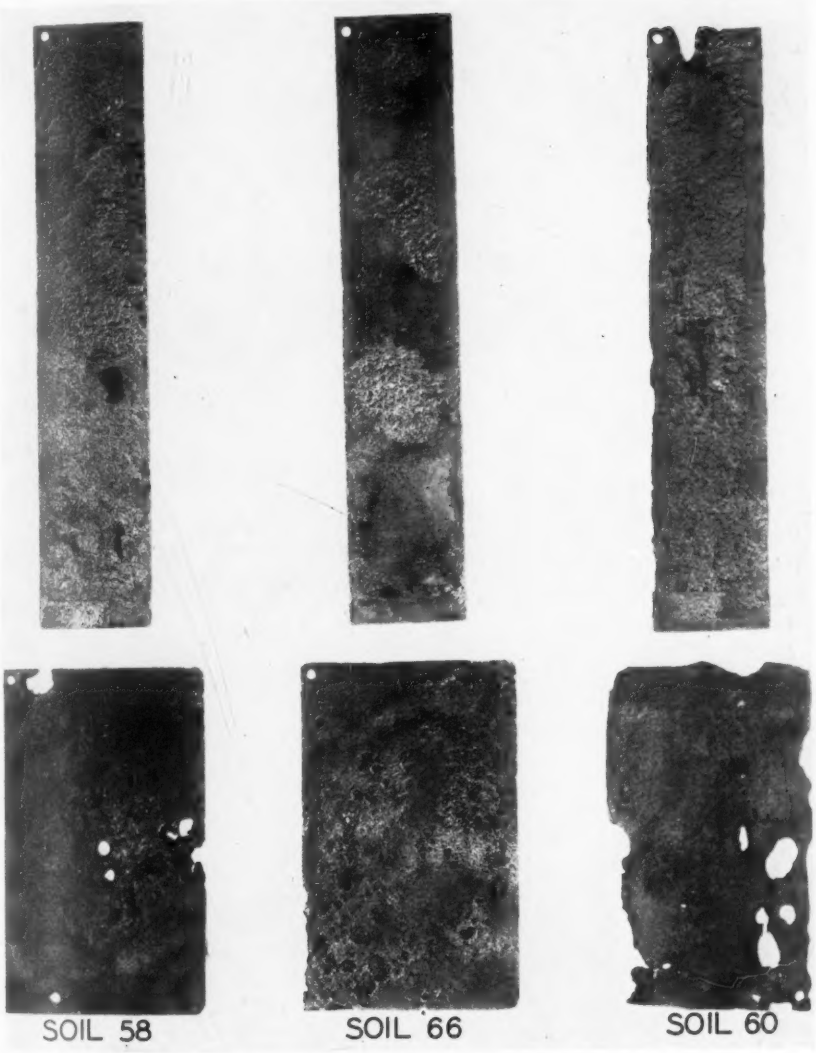

FIGURE 15.—*Rolled (above) and die-cast (below) zinc buried in muck (soil 58), in Mohave fine gravelly loam (soil 66), and in Rifle peat (soil 60), approximately 4 years each.*

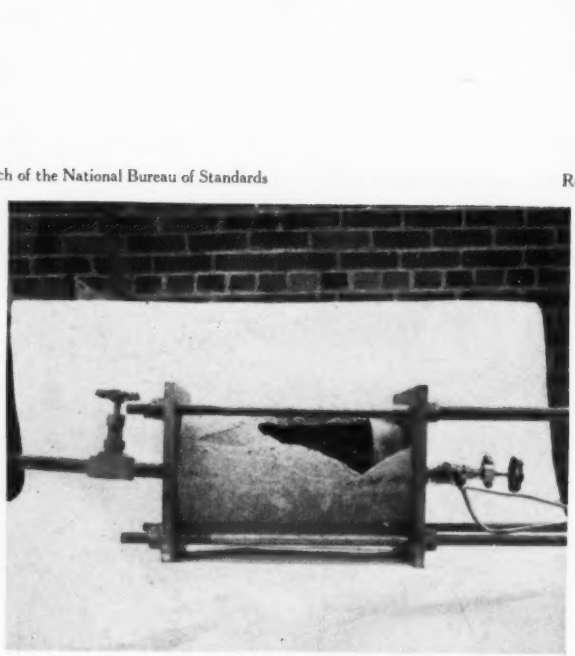

FIGURE 17.—*Bursting test apparatus.*

VI. LEAD

Three types of lead pipe were buried in 1937 for the purpose of checking the results of an earlier investigation, which tended to show that lead cable sheaths containing antimony corroded somewhat more than sheaths which did not contain this element. The sheaths also differed in source and dimensions.

Table 29 shows the dimensions and composition of lead pipe specimens buried in 1937. The ends of the pipes were closed. Table 30 shows the loss of weight and maximum penetration of the lead specimens after exposures of 2 years and of 4 years. Attention is called to the fact that the pit-depth data for the 2-year specimens has been modified from that previously reported [2]. Because of the softness of the lead pipe, most of the specimens became dented and deformed, and they acquired many tool marks during their removal from the test sites. A recent check of the pit-depth measurements indicated that in many cases pits were recorded that were actually due to the handling of the pipes after they had been removed from the test sites. Therefore, the data in table 30 are to be taken as superseding the data previously published in table 22 of Research Paper RP1460.

TABLE 29.—*Dimensions and composition of lead specimens*

Material	Identification	Diameter	Length	Wall or coating thickness	Cu	Bi	Sb	Sn	Te
		in.	*in.*	*in.*	%	%	%	%	%
Chemical lead	*O*	1.5	12	0.177	0.056	0.002	0.0011	None	
Tellurium lead	*T*	1.5	12	.177	.082	None	.0011	do	0.043
Antimonial lead	*B*	1.5	12	.177	.036	.016	5.31	do	
Lead-coated steel	*CA*	1.5	13	.00144				1.00	

The data in table 30 do not show any significant difference for the three varieties of lead pipe. This is not in agreement with the conclusions based on the 2-year exposures [2], where the data indicated a slight improvement by the addition of 5 percent of antimony to the lead. It will be seen in general that soils that are severely corrosive to iron are usually noncorrosive to lead; the chief exceptions are the highly organic soils, such as soils 58 and 61. The corrosion resistance of lead can be attributed partly to the formation of insoluble compounds on the metal, which protect it from further attack in soils high in salts, such as sulfates, chlorides, and carbonates. The organic salts of lead in organic soils are usually soluble.

TABLE 30.—*Loss of weight and maximum penetration of lead pipe exposed 2 and 4 years*

Soil		Chemical lead [a]				Tellurium lead [b]				Antimonial lead [c]				Black iron pipe exposed 4 years	
		Loss of weight		Maximum penetration		Loss of weight		Maximum penetration		Loss of weight		Maximum penetration		Loss of weight	Maximum penetration
No.	Type	2 years	4 years	2 years	4 years	2 years	4 years	2 years	4 years	2 years	4 years	2 years	4 years		
		oz/ft²	*oz/ft²*	*Mils*	*Mils*	*oz/ft²*	*oz/ft²*	*Mils*	*Mils*	*oz/ft²*	*oz/ft²*	*Mils*	*Mils*	*oz/ft²*	*Mils*
53	Cecil clay loam	0.22	0.21	18	12	0.25	0.31	12	20	0.25	0.22	10	10	2.86	98
55	Hagerstown loam	.37	.20	24	26	.34	.28	26	26	.19	.15	26	18	2.60	50
56	Lake Charles clay	.21	.45	38	37	.38	.82	30	48	.31	.50	39	52	16.03	104
58	Muck	1.56	2.41	34	28	1.68	2.80	55	56	1.45	2.12	50	58	8.78	46
60	Rifle peat	0.18	0.28	18	15	0.15	0.20	29	10	0.10	0.22	6	[d] *P*	8.06	38
61	Sharkey clay	1.46	2.21	35	39	1.21	1.75	33	30	.94	1.75	31	42	4.99	45
62	Susquehanna clay	0.30	0.93	32	29	0.36	0.64	19	31	.27	1.03	12	30	4.30	56
63	Tidal marsh	.054	.015	14	18	.056	[e] .015	10	[e] 12	.038	0.013	*P*	16	9.20	38
64	Docas clay	.20	.19	24	16	.25	.18	21	11	.12	.19	12	12	5.96	67
65	Chino silt loam	.14	.13	40	24	.17	.16	22	16	.17	.21	6	15	4.56	59
66	Mohave fine gravelly loam	.10	.10	44	34	.25	.12	23	41	.063	.12	12	15	12.31	[f] 145+
67	Cinders	3.67	12.21	79	104	3.35	13.22	71	94	3.14	4.21	56	90	[g] 37.03	145+
69	Houghton muck	0.36	0.81	21	15	0.23	1.08	8	12	.20	1.04	9	7	3.28	20
70	Merced silt loam	.034	.12	48	14	.094	0.15	16	27	.10	0.14	11	12	9.72	118+

[a] Cu, 0.056%; Bi, 0.002% Sb, 0.0011%.
[b] Cu, 0.082%; Te, 0.043%; Sb, 0.0011%.
[c] Cu, 0.036%; Bi, 0.016%; Sb, 5.31%.
[d] *P* indicates definite pitting but no pits greater than 6 mils.
[e] Data for 1 specimen only.
[f] + indicates a hole in 1 or both specimens due to corrison.
[g] Data for 1 specimen only. The other specimen was destroyed by corrosion.

VII. ASBESTOS-CEMENT PIPE

Asbestos-cement pipe is a mixture of asbestos-fiber and cement. The pipe is built up by a continuous process on a revolving steel mandrel. This is followed by a curing process. Since asbestos-cement pipe is nonmetallic, it is, of course, not subject to galvanic corrosion, tuberculation, or electrolysis. Pipe of this type is manufactured largely for use in transmission mains and services where the working pressures range from 50 to 200 pounds per square inch.

In order to determine whether asbestos-cement pipe is subject to deterioration under soil conditions, specimens were buried at 15 test sites in 1937. The specimens were 12 inches long, 6 inches in diameter, and had an average wall thickness of 0.72 inch. These specimens were cut from class 150 pipe. Two specimens were removed from each test site at each inspection period, after exposure for 2 and for 4 years. In most soils, especially in the acid soils, there was some softening of the surface of the specimens. However, scratching into the specimens showed this softening to be superficial. The softening probably occurred only on the outer layers of the asbestos-cement sheet that were applied to the pipe without pressure during the manufacturing process in order to remove the pipe from the press section. The material immediately under the softened outer layers appeared to be of the same density as the rest of the specimen. In order to measure any change that may have taken place during exposure to the soil, the specimens were subjected to water absorption, density, crushing, and bursting tests. Five representative samples from the group of specimens were stored at the National Bureau of Standards and were subjected to the same tests.

Before the various tests were made on the buried specimens, the 2- and 4-year sets were exposed to the air for 4 years and for 2 years, respectively. What effect, if any, this may have had on the results of the tests is not known at present, but a possible explanation may be had from future removals when the specimens will probably be tested immediately after removal from the test sites. In order to reproduce approximately the conditions of the pipe in the soil, the specimens were immersed in water for a least 48 hours previous to making the crushing and bursting tests.

1. WATER-ABSORPTION TEST

Weighed air-dried specimens were immersed in water at room temperature for certain periods of time, after which they were removed and wiped with a damp cloth and reweighed. Water absorption was expressed as the percentage gain in weight. The results are tabulated in table 31.

TABLE 31.—*Absorption of water by asbestos-cement pipe*

Soil No.	Specimen No.	Water absorption—percentage gain in weight				
		1 day	2 days	3 days	4 days	14 days
2-YEAR-OLD SPECIMENS						
51	41		1.64	1.87		3.68
53	68		2.13	2.74		6.75
55	149		1.86	2.35		6.76
56	39		.86	.97		1.66
58	21		3.08	3.86		7.49
60	71		5.21	6.26		10.18
61	12		1.13	1.36		2.79
62	56		1.55	1.81		3.65
63	1		1.50	1.97		4.25
64	111		1.15	1.31		2.70
65	121		1.58	1.69		
66	99		1.11	1.37		
67	131		1.00	1.25		3.99
69	89		1.96	2.48		4.42
70	101		2.05	2.40		5.10
4-YEAR-OLD SPECIMENS						
53	67	1.69	2.26		3.04	
55	147	1.75	2.58		3.80	
56	31					
58	26	2.53	3.14		3.57	
60	74					
61	13	1.37	1.54		1.80	
62	57	2.45	3.77		5.22	
63	9					
64	119	.82	1.02		1.18	
65	128					
66	97	1.85	2.04		2.34	
67	133	1.35	1.77		2.11	
69	87	2.14	2.61		3.24	
70	109					
UNBURIED SPECIMENS						
	2		4.73	5.69		
	3		5.96	7.26		

There is no evident consistency in the amount of water absorbed by the specimens as a group, or by the individual specimens buried in the same soil and removed during different periods. Figure 16 shows some of the representative curves obtained from the data. The curves indicate that the unburied specimens absorbed more water than did the buried specimens, with the possible exception of the 2-year specimen from soil 60.

2. CRUSHING TESTS

The crushing tests were made on 5¾-inch lengths of pipe prepared by cutting in half each specimen that had been used for the water-absorption tests. After being air-dried these sections were immersed in water for 48 hours. The tests were made with three-edge bearings according to the method described in the Federal specifications for asbestos-cement pipe. Each section was placed in a horizontal position on lower bearings consisting of two wooden strips with vertical sides, each strip having its interior corner rounded to a radius of approximately ½ inch. The strips were securely fastened to a rigid wooden block with their interior vertical sides 1 inch apart. The

upper bearing consisted of a straight wooden block, 4 by 4 inches in cross section. The load was applied at a uniform rate of approximately 1,000 pounds per minute until failure of the pipe occurred. In testing the specimens, the two sections from the same specimen were placed under the hydraulic jack in such a way that the parts of the sections receiving the maximum stress were at an angle of 90° to each other.

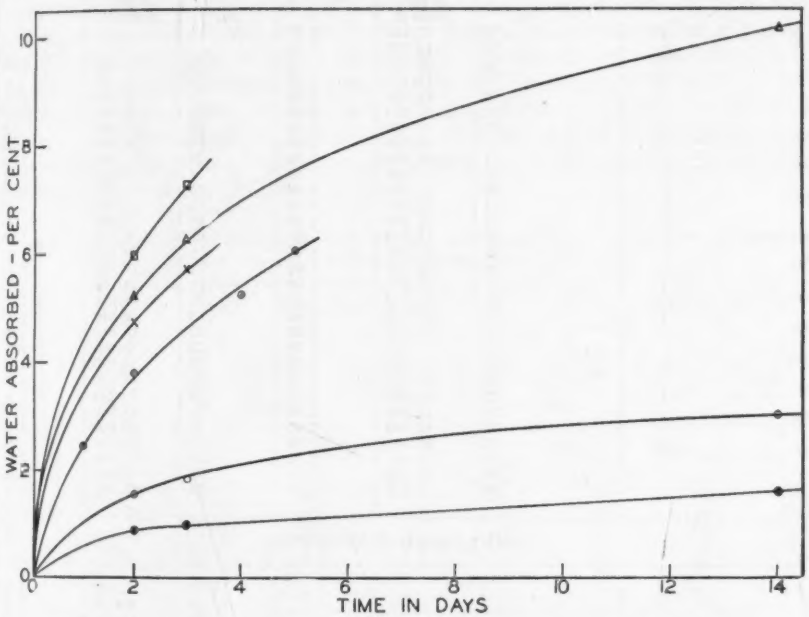

FIGURE 16.—*Percentage of water absorbed by asbestos-cement specimens.*

●=Exposed 2 years to soil 56.
○=Exposed 2 years to soil 62.
⊙=Exposed 4 years to soil 62.
△=Exposed 2 years to soil 60.
×=Unexposed.
□=Unexposed.

The crushing strengths in pounds per linear foot for each of the sections were calculated. The results of these tests are given in table 32 for the specimens exposed to the soil and for the unexposed specimens. No evident correlation is shown between the value for the crushing strength and the age of the specimens either in individual soils or as any group of soils.

TABLE 32.—*Results of crushing tests on the asbestos-cement specimens exposed to various soils and on the unexposed specimens*

Soil No.	Sample	2-year-old specimens			4-year-old specimens		
		Minimum wall thickness	Crushing strength	Apparent specific gravity	Minimum wall thickness	Crushing strength	Apparent specific gravity
		in.	*lb per linear ft*		*in.*	*lb per linear ft*	
51	*a*	0.76	12,160	1.90			
	b	.76	12,720	1.90			
53	*a*	.72	13,910	1.90	0.70	11,400	1.91
	b	.72	14,400	1.96	.70	10,290	1.90
55	*a*	.69	13,200	1.86	.70	12,590	1.93
	b	.69	11,070	1.78	.70	13,160	1.97
56	*a*	.71	12,930	1.94	.70	12,380	1.94
	b	.71	13,350	1.94	.70	12,800	1.99
58	*a*	.71	11,970	1.89	.74	12,240	1.84
	b	.71	13,550	1.89	.74	12,290	1.91
60	*a*	.70	12,730	1.88	.73	12,670	1.91
	b	.72	11,520	1.82	.73	11,580	1.90
61	*a*	.73	14,600	1.90	.67	9,840	1.98
	b	.73	15,270	1.89	.67	9,550	1.93
62	*a*	.73	17,060	1.94	.71	12,980	1.91
	b	.73	14,240	1.92	.71	12,980	1.94
63	*a*	.77	17,600	1.80	.71	14,990	1.92
	b	.77	17,150	1.86	.71	14,980	1.99
64	*a*	.72	15,400	1.93	.73	14,640	1.93
	b	.72	13,430	1.96	.73	15,940	2.00
65	*a*	.71	15,560	1.92	.73	13,290	1.91
	b	.71	16,400	1.92	.73	13,040	1.94
66	*a*	.72	14,470	1.95	.69	14,160	1.88
	b	.72	14,530	1.97	.69	13,210	1.87
67	*a*	.73	15,900	1.94	.70	11,650	1.92
	b	.73	15,400	1.94	.70	10,640	1.85
69	*a*	.70	13,100	1.88	.71	11,920	1.88
	b	.70	11,000	1.82	.71	11,540	1.84
70	*a*	.70	12,400	1.91	.73	15,440	2.02
	b	.70	13,960	1.94	.73	13,080	1.99
UNEXPOSED SPECIMENS							
4	*a*				0.70	9,940	1.92
	b				.70	10,270	1.90
5	*a*				.71	11,840	1.90
	b				.71	10,530	1.90
Average of unexposed specimens					.70	10,640	1.91

3. BURSTING TESTS

For the bursting tests the second of the pair of specimens removed from each test site at each inspection period was immersed in water for a minimum of 48 hours, and placed in the hydrostatic-pressure testing apparatus shown in figure 17. Internally fitting rubber cups were used to close the ends of the pipe. The apparatus was so designed that the pipe was not subjected to end compression during the test. After filling the pipe under test with water, the entrapped air was allowed to escape, and the pressure was increased at an approximate rate of 10 pounds per square inch per second until the pipe failed. The pressure gage employed was calibrated before the series of tests.

Many samples failed by a small piece splitting out at one end with the extension of a crack from this point along the entire length of the specimen. The others failed by cracking in one or two places along the entire length of the specimen. In all but three cases, a crack went through a hole, $\frac{1}{16}$-inch in diameter, near one end of the specimen,

which was used to hold the identification tag. Here again there is no evident correlation between the bursting pressure and the age of the specimens either in individual soils or as any group of soils.

4. APPARENT SPECIFIC GRAVITY

Samples from the specimens upon which the crushing and bursting tests had been made were dried in an oven at about 110° C for 18 hours. After cooling to room temperature the weight of the dry sample was determined. The samples were then immersed in water for a period of 24 hours, and the weights in the wet condition were determined in air and when submerged in water. From the original weights of the dry samples and the volume of water displaced, the apparent specific gravities of the specimens shown in tables 32 and 33 were calculated. With few exceptions, the specific gravity of the specimens all fall between the values of 1.80 and 2.00.

TABLE 33.—*Results of bursting tests on the asbestos-cement specimens exposed to the various soils and on the unexposed specimens*

Soil No.	2-year old specimens			4-year old specimens		
	Minimum wall thickness along fracture	Bursting pressure	Apparent specific gravity	Minimum wall thickness along fracture	Bursting pressure	Apparent specific gravity
	in.	*lb/in.²*		*in.*	*lb/in.²*	
51	0.71	995	1.89			
53	.75	1,140	1.83	0.71	1,010	1.84
55	.72	1,085	1.87	.72	1,100	1.77
56	.70	995	2.00	.73	1,050	1.84
58	.73	1,140	1.76	.71	925	1.90
60	.71	1,010[a]	1.76	.72	1,165	1.85
61	.71	1,205	1.92	.71	1,065	1.94
62	.73	1,095	1.97	.70	1,125	1.78
63	.75	1,175	1.84	.74	1,150	1.88
64	.67	1,100	1.98	.74	1,150	1.94
65	.69	935	1.76	.70	1,070	1.84
66	.75	1,215	1.93	.71	1,240	1.89
67	.72	1,030	1.86	.73	1,105	1.82
69	.74	1,255	1.93	.68	1,215	1.89
70	.72	1,155	1.80	.77	1,285	1.84
UNEXPOSED SPECIMENS						
1				0.71	995	1.81
2				.72	940	1.88
3				.73	970	1.93
Average of unexposed specimens				.72	968	1.87

5. COMPARISON OF THE DATA FROM VARIOUS TESTS

Analysis of the data in tables 31 to 33 fails to bring out any correlation between any of the tests. The bursting- and crushing-test data for the specimens exposed for 2 and for 4 years do not show any evident differences. In some soils the 2-year specimens appear superior to the specimens exposed 4 years, and in other soils the reverse is true. No systematic differences between specimens exposed to different soil conditions can be detected.

However, the data do indicate that the asbestos-cement pipes generally gained strength during exposure to the soil, and that the softening observed on the outer layers of the specimens did not pene-

trate deeply. For only two specimens are the values for the bursting pressure less than the maximum value of the unexposed specimens, and in only one soil are both values of the crushing strength for the exposed specimens less than the average value of the unexposed specimens. It is probable that during exposure of asbestos-cement pipe to the soil, a curing process takes place which tends to increase the strength of the pipe, but there is no indication that the pipe is any stronger after 4 years of exposure than after 2 years of exposure.

VIII. METALLIC COATINGS

1. TINNED-COPPER TUBES

Table 34 shows the loss of weight and maximum penetration of tinned-copper tube exposed for 4 years and similar data on deoxidized copper pipe exposed at the same test sites for 5 years. The table shows that in general the coating of tin temporarily reduced the rate of loss of weight but, in some cases at least, accelerated the rate of maximum penetration. The coating of tin was quite thin, and much of it had disappeared from the specimens buried in most of the soils.

TABLE 34.—*Loss of weight and depth of maximum penetration of tinned-copper tubes exposed 4 years and copper pipe exposed 5 years*

M, shallow metal attack as indicated by roughening of the surface.
P, definite pitting but no pits greater than 6 mils.
+, one or both specimens contained holes caused by corrosion.

Soil		Tinned-copper tube			Deoxidized copper pipe			Condition of coating [a]
No.	Type	Exposure	Loss of weight	Maximum penetration	Exposure	Loss of weight	Maximum penetration	
		Years	*oz/ft²*	*Mils*	*Years*	*oz/ft²*	*Mils*	
53	Cecil clay loam	4.01	0.086	7	5.46	0.15	7	1
55	Hagerstown loam	3.90	.11	*M*	5.20	.14	*P*	0
56	Lake Charles clay	3.99	.36	11	5.44	.51	*P*	2
58	Muck	4.01	.64	39	5.50	1.56	12	2
60	Rifle peat	3.98	4.54	42	5.25	3.82	28	3
61	Sharkey clay	4.01	0.32	[b] 18(2)	5.50	0.35	23	2
62	Susquehanna clay	4.00	.081	*P*	5.47	.26	9	1
63	Tidal marsh	4.01	2.19	[c] 14	5.55	2.45	*M*	3
64	Docas clay	3.98	0.22	6	5.22	2.22	9	2
65	Chino silt loam	3.99	.12	*P*	5.26	1.02	10	1
66	Mohave fine gravelly loam	3.95	.23	*P*	5.28	0.75	7	2
67	Cinders	3.98	20.37	60+(2)	5.26	9.33	54	3
69	Houghton muck	3.98	[d] 0.23	*P*				1
70	Merced silt loam	3.98	.074	6				1

[a] 0, Coating, present over entire surface;
1, Coating present on more than 50% of surface;
2, Coating present on less than 50% of surface;
3, Little or no coating left.
[b] (2) Indicates that 1 of the specimens was punctured after 2 years exposure.
[c] Uniform corrosion; no reference surface left.
[d] Data for 1 specimen only.

Aside from the question of minimum thickness required for protection, a possible cause of failure of tinned-copper in soils is the reversal of potential of this couple. As tin is probably anodic to copper under all conditions, corrosion of tin would be expected to protect copper cathodically in the same manner that the corrosion of zinc protects the underlying steel in galvanized materials. The reversal of potential may be due to the formation of tin-copper alloys, which have been shown under certain condition to be more cathodic than copper [21].

2. LEAD

Table 35 shows the loss of weight and depth of maximum penetration of lead-coated and uncoated steel pipe exposed for 9 years. In all cases the coating reduced the loss of metal, and in 9 of the 13 soils the maximum penetration was also reduced. However, rather serious pitting occurred in all but one of the soils. Since lead, unlike zinc, is cathodic to iron and steel, protection of the underlying metal is accomplished by isolating the base metal from the enviornment. The life of the coating would then be expected to be determined largely by the corrodibility of lead under the conditions of exposure. Furthermore, if the corrosion of lead in soils takes the form of localized attack, or pitting, the potential difference between lead and the exposed steel would cause accelerated attack on the steel except under those conditions in which the steel might be polarized anodically. The average thickness of the lead coating was 1.44 mils. The corrosion for the three types of lead specimens shown in table 30 indicates that the protection provided by a coating of this thickness would be inadequate, since in all soils the maximum penetration of the lead pipe after 2 years' exposure to the same soil conditions exceeded the average thickness of the lead coating on the pipe specimens. It is doubtful that a lead coating of any reasonable thickness could be considered satisfactory for use in corrosive soils.

TABLE 35—*Loss of weight and depth of maximum penetration of lead-coated and steel pipe exposed for 9 years*

Soil		Lead-coated [a] *CA*		Low-carbon steel *N*		Condition of coating [b]
No.	Type	Loss of weight	Penetration	Loss of weight	Penetration	
53	Cecil clay loam	[c] 1.12	41	4.09	59	2
55	Hagerstown loam	0.76	44	3.82	59	1
56	Lake Charles clay	20.73	[d] 145+(7)	28.76	154+(7)	3
58	Muck	14.85	[c] 91	16.24	[c] 110	3
59	Carlisle muck	1.07	[f] 21	4.70	[f] 40	1
60	Rifle peat	[f] 7.07	50	16.72	[c f] 27	3
61	Sharkey clay	3.89	50	5.78	[f] 96	2
62	Susquehanna clay	3.64	59	6.65	[f] 87	3
63	Tidal marsh	[c] 3.52	[c] 145+	[f] 9.03	54	2
64	Docas clay	2.10	73	[e] *D*	154+(5,7)	2
65	Chino silt loam	3.22	72	12.86	112	2
66	Mohave fine gravelly loam	3.39	57	18.56	154+(5,7)	2
67	Cinders	*D*	145+(5,7)	[h] 58.39	154+(2,5,7)	3

[a] This coating was 0.00144 inch thick, and contained 1 percent of tin.
[b] 1, Coating on more than 50 percent of surface; 2, coating on less than 50 percent of surface; 3, little or no coating left.
[c] Data for only 1 specimen.
[d] + indicates that 1 or both specimens punctured. A number in parentheses after the pit depth indicates that 1 or both specimens were punctured in previous removals, e. g., (5) indicates a puncture after 5 years, etc.
[e] Uniform corrosion; no reference surface left on pipe.
[f] Data for individual specimens differed from the average by more than 50 percent.
[e] *D* = both specimens destroyed by corrosion.
[h] Data for 1 specimen only; the other specimen was destroyed.

3. ZINC

Zinc applied by the hot-dip method has been used extensively for the protection of small-diameter pipes under ground and its long-continued use is evidence of its value under average conditions. In 1937, steel specimens with a zinc coating having a weight of 3.08 ounces per square foot were buried at the 15 test sites previously men-

tioned. The condition of these specimens after 4 years is reported in table 36. Figure 18 shows the galvanized and black-iron pipes that were buried as control specimens at three test sites. In all but one of the soils pitting began within the 4-year period, and the coating, including the zinc-iron alloy layer, was removed from at least half of the surface of the specimens. Under these conditions it seems probable that a zinc coating of the thickness and distribution of the one tested would not add more than 4 years to the life of a pipe exposed to the soils under observation. This result is inconsistent with the data of previous described tests [16], in which a coating of 2.82 ounces per square foot prevented pitting of the base metal in all but one of 47 soils over a 10-year period. Although certain of the soils in the more recent series of tests proved to be more corrosive than the soils in the older tests, it also is true that six soil conditions were duplicated in the two series of tests.

TABLE 36.—*Loss of weight and depth of maximum penetration of galvanized and black iron pipe exposed 4 years*

Soil		Galvanized pipe 3.08 oz/ft²		Black iron pipe		Condition of coat [a]
No.	Type	Loss of weight	Penetration	Loss of weight	Penetration	
		oz/ft²	*Mils*	*oz/ft²*	*Mils*	
53	Cecil clay loam	1.39	6	2.86	98	2
55	Hagerstown loam	[b] 1.22	8	2.60	50	2
56	Lake Charles clay	3.89	7	16.03	104	2
58	Muck	5.40	[b] 21	8.78	46	3
60	Rifle peat	7.18	12	8.06	[b] 38	3
61	Sharkey clay	1.46	12	4.99	45	2
62	Susquehanna clay	2.28	9	4.30	56	2
63	Tidal marsh	2.15	10	9.20	38	1
64	Docas clay	1.58	9	5.96	67	2
65	Chino silt loam	[b] 2.25	6	4.56	59	3
66	Mohave fine gravelly loam	3.32	8	12.31	[c] 145+(2)	2
67	Cinders	5.40	45	[d] 37.03	145+(2)	3
69	Houghton muck	3.37	11	3.28	20	3
70	Merced silt loam	4.52	12	[b] 9.72	118+	3

[a] 1, Coating on more than 50 percent of surface; 2, coating on less than 50 percent of surface; 3, little or no coating remaining.
[b] Data for individual specimens differed from each other by more than 50 percent.
[c] + indicates hole in 1 or both specimens caused by corrosion; (2) indicates that 1 or both specimens were punctured after 2 years' exposure.
[d] Data for 1 specimen; the other specimen was destroyed.

It was thought that the difference in behavior of the specimens having coatings of nominally the same thickness might possibly be ascribed to greater uniformity in distribution of the zinc coating in the earlier tests. However, measurements made with a Magne-gage on three unburied representative samples of the specimens from the earlier tests and on four similar specimens from the more recent tests showed that the variations in the thickness of the coatings on the pipe were no greater on one group than the other. Hence, the difference in behavior of the two specimens cannot be attributed to differences in uniformity of the zinc layers.

IX. NONBITUMINOUS ORGANIC COATINGS

The value of the tests of organic coatings applied to short length of pipe under laboratory conditions is limited because many of the failures of coatings in practice are attributable to injuries in the course

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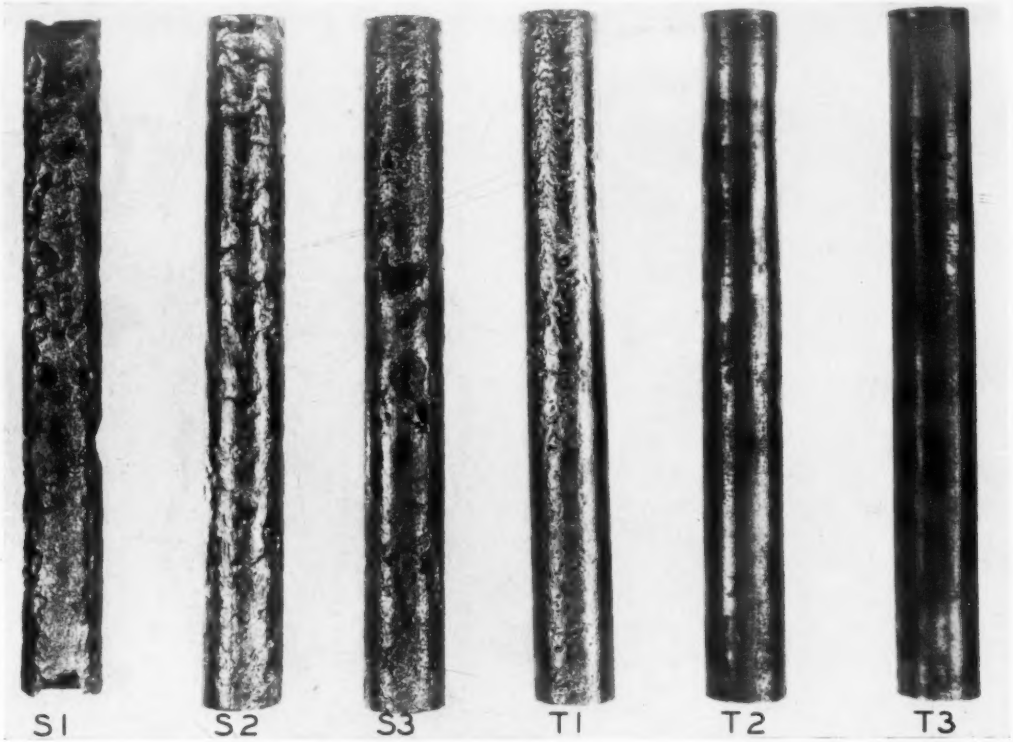

FIGURE 18.—*Black iron (S) and galvanized (T) pipes buried approximately 4 years in cinders (S1) and (T1), Lake Charles clay (S2) and (T2), and Mohave fine, gravelly loam (S3) and (T3).*

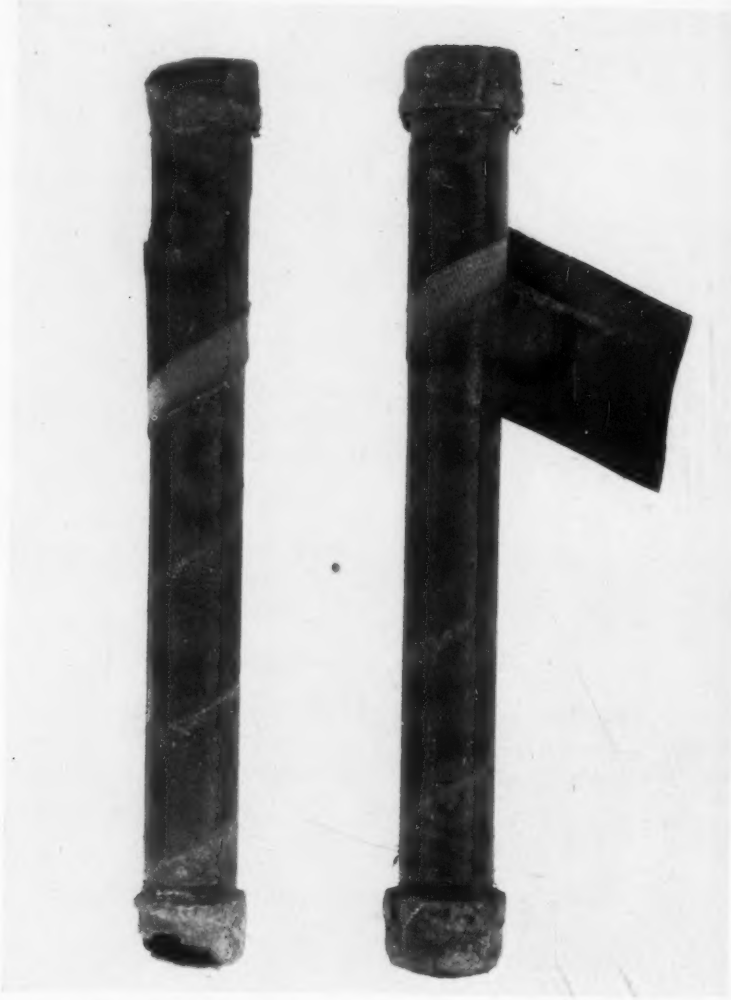

FIGURE 19.—*Koroseal-coated pipe exposed for 4 years to cinders (soil 67).*

of the laying of the coated line. Moreover, it is difficult to produce a uniform coating in the field and even in the shop.

Such tests as are reported here are chiefly of value in that they show whether or not there is a possibility that a satisfactory coating could be made from the material tested. The tests may also suggest ways in which coatings could be improved. Most of the organic coatings reported on are either experimental or else materials which have been satisfactory under some conditions but are untried with respect to underground pipes. Few, if any, are in use in an experimental way on short sections of lines.

When the coated specimens were removed the coatings were examined for cracks, blisters, brittleness, change in color, and disbonding, as well as for rust spots and other evidence that corrosion had not been entirely prevented. Half of the coating was then removed and the extent of the corrosion, if any, recorded.

As it is frequently impossible to describe the condition of a coating accurately and briefly, and since the chief function of a coating for use in soil is to prevent corrosion, it has become customary to limit the report on organic coatings to a description of the condition of the pipe which they were intended to protect. This is not entirely satisfactory, as the depth of penetration is a function of the corrosiveness of the soil and probably nearly independent of the coating after the metal surface has been exposed. The seriousness of the corrosion may, however, indicate roughly the lapse of time since the surface became exposed if the corrosiveness of the soil is known. Even this is somewhat in doubt, since there is considerable evidence that under some conditions a faulty coating may accelerate corrosion either by localizing the corroding current or by modifying the differential aeration of the metal. Until recently many have regarded the usefulness of a coating as limited to the time during which it prevents corrosion. Experience has shown that with most coatings it is impractical to protect all points on a pipe surface because of accidents inherent in the application of the coating, the laying of the pipe line, root growth, or other injuries. Under most conditions it is practicable to protect electrically cross-country pipe lines, and possibly city pipe networks as well, by causing sufficient current to flow to the pipe. The cost of this method of preventing corrosion (cathodic protection) is roughly proportional to the current required and this is in turn proportional to the insulating properties of the protective coating. Thus a combination of protective coating and cathodic protection may be more economical than complete protection by either method alone. Under some conditions it may be more economical to permit a limited amount of corrosion than to prevent all of it. This, of course, depends on the losses assignable directly and indirectly to corrosion. It is from this point of view that pipe coatings should be judged.

1. COATINGS EXPOSED FOR 9 YEARS

The only information available descriptive of the coatings buried in 1932 was furnished by the manufacturers and is given below.

Coating B.—A synthetic rubber, stated to be an olefin polysulfide reaction product, was exposed in the form of sheets 10 by 5 by 1/4 inches. Subsequently, a process was developed which permitted application of this material to pipes. Specimens coated by this

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process were exposed in 1939 and inspected in 1941. The condition of these coatings will be described in the section under coatings exposed for 2 years.

Coating C.—Two coats of porcelain enamel, one of which was acid-resisting. Thickness, 14 mils.

Coating D.—First coat, 23-percent solution of a rubber derivative in xylene; second and third coats, 30-percent solution of the rubber derivative in xylene; fourth coat, 20-percent solution of the rubber derivative in a mixture of turpentine and mineral spirits. Five percent of the solids was carbon black. Thickness, 10 mils.

Coating E.—Two applications of paint which differed in color. Neither the kind of pigment nor the kind of vehicle was specified. Thickness, 5 mils.

Coating F.—A semiplastic compound, which was applied cold with a brush, consisting of 4½ parts of treated cashew-nutshell oil, 3 parts of asbestos fiber, and 3½ parts of mineral turpentine substitute. Thickness, 6 mils.

Coating G.—A hard-rubber compound, containing rubber, sulfur, and an accelerator, cured to a bone-hard condition. Thickness, 90 mils.

Coating H.—A highly loaded hard-rubber stock that contained 30 percent of magnesium carbonate and approximately 15 percent of "white substitute." Thickness, 100 mils.

Coating J.—A synthetic resin varnish baked at 425° F for 30 minutes.

Coating K.—A paint containing highly chlorinated rubber, dissolved in a suitable solvent, to which may have been added drying oils, pigments, quartz meal, or carborundum. This coating was applied in Germany to pipe 1 inch in outside diameter. Thickness, 6 mils.

Coating W.—An experimental coating prepared as follows: The pipe was primed with a china-wood oil varnish containing zinc chromate and baked at 200° F for ½ hour. A top coat of dehydrated china-wood oil, containing powdered mica and a catalyst, was molded on the pipe and heated to 200° F for 3 hours. Thickness, 170 mils.

Table 37 shows the condition of the pipe beneath the coatings exposed for 9 years. It will be noted that the two thick rubber coatings, *G* and *H*, completely protected the pipes except at the ends where the coating had been injured mechanically. The porcelain enamel was nearly as good. It is probable that some of the corrosion reported was the result of injuries in handling of the specimens. It is claimed by the manufacturer that great strides have been made in resistance to chippage of porcelain enamel coatings during the past 9 years, and that the samples reported upon would not be truly representative of the type of porcelain enameling which would be obtainable today. However, as much greater care was taken than is practical with coatings on pipe lines, the corrosion resulting from injuries should not be entirely neglected.

The thick china-wood oil compound, *W*, prevented serious pitting in all soils. The fact that many of the coatings cracked and had a strong odor and the blistering of the priming coat indicate that the coating has deteriorated. However, because of its thickness it may continue to be helpful by isolating the pipe from the soil for several more years. The thin coatings (*D*, *E*, *F*, *J*, and *K*) have definitely deteriorated and are probably of little further use. Most of these coatings showed evidence of breakdown on earlier examinations.

TABLE 37.—*Condition beneath nonmetallic coatings exposed for 9 years*

[Figures indicate depths of maximum pits in mils]

E, ends corroded
G, ends rusted.
H, pipe punctured, 145+ mils.
M, metal attack—pipe roughened by corrosion.
R, pipe rusted.
P, definite pitting but no pits greater than 6 mils.
U, no corrosion.
D, pipe destroyed by corrosion.

Soil		Specimen No.	Porcelain enamel	Rubber paint	Paint	Cashew-nut-oil-asbestos fiber	Hard rubber	Loaded hard rubber	Synthetic resin	Chlorinated rubber paint	China wood-oil mica compound	Uncoated low-carbon steel pipe
No.	Type		*C*	*D*	*E*	*F*	*G*	*H*	*J*	*K*	*W*	*N*
53..	Cecil clay loam	1	*U*	*M*	17	*M*	----	----	*M*	16	*M*	59
		2	*UE*	9	15	*R*	----	----	*M*	24	*M*	59
		3								27		
55..	Hagerstown loam	1	*R*	*M*	16	*R*	----	----	----	----	*M*	48
		2	*U*	*M*	28	*R*	----	----	----	----	*M*	70
56..	Lake Charles clay	1	*UE*	[a]51	[b] *H*(7)	*M*	----	----	----	----	*M*	*H*(154+)(7)
		2	*ME*	[a]38	[a]104	*M*	----	----	----	----	*M*	*H*(154+)
58..	Muck	1	54*E*	53	97	61	----	----	----	----	*M*	[a]122
		2	*R*	52	*H*(7)	*R*	----	----	----	----	*R*	[a]98
59..	Carlisle muck	1	*U*	19	*P*	*M*	*U*	*U*	----	----	*M*	25
		2	*U*	*M*	15	*R*	*U*	*U*	----	----	*M*	54
60..	Rifle peat	1	*U*	15	[a]38	31	*U*	*U*	----	----	*M*	18
		2	*UE*	[a]44	[a]25	*R*	*U*	*U*	----	----	*M*	[a]36
61..	Sharkey clay	1	*U*	*R*	58	*R*	----	----	----	----	*M*	130
		2	*U*	*U*	48	*R*	----	----	----	----	*MG*	62
62..	Susquehanna clay	1	*U*	*U*	27	*R*	----	----	----	----	*MG*	121
		2	*U*	23	25	27	----	----	----	----	*M*	53
63..	Tidal marsh	1	*UE*	*M*	----	*P*	----	----	----	----	----	44
		2										65
64..	Docas clay	1	*RE*	37	*D*(7)	*M*	*UE*	*M*	[a]122	52	*M*	*H*(154+)(5, 7)
		2	*UE*	47	*D*	*M*	*UG*	*U*	[a]125	60	*R*	*H*(154+)
65..	Chino silt loam	1	*U*	12	*D*(7)	*P*	*UE*	*U*	----	----	*MG*	118
		2	*U*	11	[a]87	*R*	*UG*	*U*	----	----	*M*	106
66..	Mohave fine gravelly loam.	1	*UE*	29	[a]77	34	*UE*	*U*	----	----	*M*	*H*(154+)(5, 7)
		2	*U*	15	[a]122	*M*	*UE*	*UE*	----	----	*M*	*H*(154+)
67..	Cinders	1	*UE*	77	*D*(7)	16	*UE*	*UE*	*H*(7)	[a]92	*R*	*H*(154+)(2, 5, 7)
		2	43*E*	*H*	*H*	*R*	*UE*	*UG*	*H*	----	*ME*	*H*(154+)

[a] Severe uniform corrosion; no reference surface; impossible to measure true penetration.
[b] The number in parentheses after the pit depth indicates that 1 or both specimens was punctured in the previous removal indicated by the number, (5) indicates that the pipe was punctured after 5 years, etc.

COATINGS EXPOSED FOR 4 YEARS

Five different nonmetallic coatings were buried in 1937. All of these coatings were of the phenol-formaldehyde (Bakelite) type with the exception of one which was of the polyvinyl chloride resin (Koroseal) type. All the coatings were applied to pipe about 12 inches long and 1½ inches in diameter. The descriptions of the coatings follow:

Coating L.—Two coats of a Bakelite varnish followed by two coats of another type of Bakelite varnish, each coat being baked after spraying. It appears as though the baking resulted in a fusion of the separate layers. Thickness, 7 mils.

Coating M_1.—Two coats of a Bakelite primer followed by two coats of a Bakelite chemically resistant aluminum paint. Each coat was sprayed and allowed to air-dry overnight. Thickness, 4 mils.

Coating M_2.—The same as coating M_1, except that it was applied to 2½ by 12-inch plates instead of to pipe. Thickness, 3 mils.

Coating N.—A double layer of Bakelite-treated asbestos tape, the second layer overlapping the first, which was made to adhere to the pipe and to the first layer of tape by the use of an anticorrosive resin

compound. A final protective coat was used over this tape, consisting of a spray coat of the same Bakelite chemically resistant aluminum enamel as used on the M_1 specimens. Thickness, 32 mils.

Coating P.—A fabric coated on one side with Koroseal to an overall thickness of 0.03 inch. The fabric was wrapped spirally on the pipe under tension with the Koroseal next to the metal and then painted with two coats of Koroseal solution applied hot. Thickness, 33 mils.

Table 38 shows the condition of the metal beneath the coatings, and table 39 gives a summary of the behavior of the specimens in all the soils. Two coatings remained unaffected at one test site. Corrosion had started beneath the other specimens. The failures of the Bakelite coatings were usually accompanied by blistering. The failure of the Koroseal coating is characterized by a deterioration of the fabric to which the Koroseal was applied. Accelerated corrosion in some soils was observed at places beneath the fabric in the Koroseal-coated specimens. This is shown in figure 19.

3. COATINGS EXPOSED FOR 2 YEARS

In 1939 two types of coatings were buried at 14 of the test sites and and additional coating was placed at four of the sites. The following is the maker's description of these coatings:

R.—A blue basic lead sulfate phenolic resin varnish paint consisting of two coats of the following composition:

Basic lead sulfate in raw linseed oil (90% pigment)	100 lb.
Lampblack in raw linseed oil (2% pigment)	3 lb.
Chinawood oil 100% phenolic resin varnish (33 gallon length)	23.9 lb.
Thickness of the coating	0.0055 in.

S.—Plastic made of pure vegetable gum base with nondrying oils and asbestos fiber applied cold. Shielded by a spiral wrap of impregnated cotton fabric. Thickness, 0.044 inch.

T. Thiokol sprayed on; thickness, 0.035 inch. Two specimens of each type were removed from each soil in 1941. Table 40 shows the condition of each coated pipe after an exposure of 2 years. Only one specimen showed no sign of corrosion.

TABLE 38.—*Condition of metal beneath the Bakelite and Koroseal coatings exposed for 4 years*

[A number indicates the maximum pit depth in mils]

U, No corrosion.
R, Pipe rusted.
M, Metal attack pipe roughened by corrosion.
P, Definite pitting but no pits greater than 6 mils.
E, Ends corroded.

Soil No.	Specimen No.	Coating symbol					Uncoated low-carbon steel pipe 5 years
		L	M_1	M_2	*N*	*P*	*N*
53	1	*U*	*R*	*M*	*R*		47
	2	*R*	*R*	*M*	*R*		53
55	1	*U*	*P*	*M*	*R*		48
	2	18	*P*	*M*	*R*		66
56	1	*R*	*P*	58	*P*		53
	2	*R*	*P*	*M*	*P*		88
58	1	*U*	*P*	*ME*	*P*		97
	2	12	15	25	*R*		108
60	1	*R*	*P*	55	*M*		18
	2	*U*	12	*PE*	*R*		29
61	1	18	25	25	*R*		23
	2	*U*	*R*	18	*R*		85
62	1	*U*	*R*	*M*	*R*	15	66
	2	*U*	*M*	*M*	*R*	15	66
63	1	*R*	*M*	*M*	10		33
	2	*R*	*R*	*M*	13		38
64	1	*R*	*U*	*P*	*U*		154+
	2	*R*	*U*	*P*	*R*		154+
65	1	*R*	*R*	13	*R*		79
	2	*U*	*R*	*M*	*M*		69
66	1	*M*	*R*	12	*M*	12	154+
	2	22	*P*	28	*P*	*P*	154+
67	1	*R*	120	41*E*	35	45	84
	2	*R*	107	57*E*	30	50	154+
69	1	39	24	*R*	*M*	*P*	
	2	*M*	25	32	15	8	
70	1	*U*	*R*	*PE*	*P*		
	2	*R*	*R*	16	*P*		

TABLE 39.—*Summary of condition of coated pipe exposed for 4 years*

[The figures in the table refer to the number of test sites. Data from specimens buried in 14 test sites, except for *P* specimens, which were buried in 4 test sites. The poorer of the 2 specimens is reported on.]

Coating symbol	Condition of pipe				Coating blistered
	Unaffected	Rusted	Roughened	Pitted	
L	1	8	0	5	6
M_1	1	3	2	8	13
M_2	0	0	4	10	14
N	0	5	2	7	
P [a]	0	0	0	4	

[a] Poor bond between pipe and coating.

TABLE 40.—*Condition of coated pipe exposed for 2 years*

[A number indicates the maximum pit depth in mils.

M, metal attack, pipe roughened by corrosion.
R, pipe rusted.
P, definite pitting but no pits greater than 6 mils.
U, no corrosion.

Soil No.	Specimen No.	Blue basic lead-sulfate phenolic resin varnish paint	Plastic treated fiber	Thiokol	Uncoated low-carbon steel pipe
		R	*S*	*T*	*N*
53	1	*M*	*P*		27
	2	*M*	*P*		27
55	1	*M*	*P*		46
	2	*M*	*P*		42
56	1	12	25		26
	2	*M*	20		13
58	1	*M*	*P*	*R*	20
	2	*M*	*P*	*R*	16
60	1	*R*	*M*		55
	2	*R*	*M*		19
61	1	*M*	*M*	*R*	9
	2	*M*	*M*	*U*	13
62	1	*M*	10	*R*	68
	2	*M*	10	*R*	56
63	1	*M*	28		21
	2	*M*			9
64	1	*R*	*P*	*R*	122
	2	*M*	20	*R*	138
65	1	*M*	*P*		43
	2	*M*	*P*		36
66	1	55	8		71+
	2	*P*	12		61
67	1	*M*	27		154+
	2	27	29		154+
69	1	*M*	*M*		
	2	*M*	*M*		
70	1	10	8		
	2	18	8		

The blue basic lead sulfate coating *R*, blistered and became scaly. There was little adhesion between the plastic coating *S* and the pipe. The entire surface of each pipe coated with the plastic rusted. Soil indented and adhered to the coating. In most soils the coating appeared to have rotted.

On each specimen of Thiokol-coated pipe there was a network of fine cracks, which usually did not permit water to reach the pipe. In a number of cases the coating was chipped, possibly by the formation of rust beneath the coating.

X. SUMMARY

This report deals with the conditions of a large variety of ferrous and nonferrous materials and a considerable number of metallic and organic coatings exposed from 2 to 9 years to 14 corrosive soils. The primary purpose of the tests was to assist manufacturers in obtaining data on the effectiveness of their corrosion-resistant materials with respect to corrosive soils and to aid them in the development of better materials.

Although the addition of small percentages of certain alloying elements improves somewhat the resistance of ferrous alloys to some soil conditions, the improvement cannot be considered significant. Ferrous materials must contain very considerable quantities of

nickel, chromium, or other elements if they are to withstand the action of severely corrosive soils. The behavior of 4- to 6-percent-chromium steel plates exposed 4 years is in agreement with the behavior of 5-percent-chromium steel tubes exposed 9 years in that lower loss of weight and deeper pitting were observed in comparison with plain steel.

Under most corrosive soil conditions, copper and alloys high in copper are very resistant to corrosion, and the corrodibility appears to increase with the amount of zinc in the alloy. Since dezincification plays an important role in the corrosion of brasses, weight losses and pit-depth measurements do not give a true estimation of the extent of corrosion taking place in some of the brass specimens.

The addition of 0.08 percent of arsenic to Muntz metal did not prevent dezincification.

Bursting and crushing tests indicate that asbestos-cement pipe gained somewhat in strength after exposure to the soil for 4 years.

The two lead alloys corroded at about the same rate as chemical lead. The extent of corrosion on the lead-coated specimens indicates that a lead coating of any reasonable thickness can not be considered satisfactory for use in corrosive soils.

A coating of tin over copper gave little protection over a period of 4 years.

Several experimental coatings greatly reduced corrosion over periods of from 4 to 9 years. Among these are a vitreous enamel, two thick rubber coatings, a thick molded coating of china-wood oil and mica, and a thin baked-on Bakelite coating (4 years).

The thin coatings, of which there were several, reduced corrosion but showed distinct signs of deterioration and cannot be considered adequate for severe soil conditions.

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U. S. Department of Commerce National Bureau of Standards

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REVISED RESULTS OBTAINED WITH CERTAIN DEHYDRATING AGENTS USED FOR DRYING GASES

By John H. Bower

ABSTRACT

This paper is a revision of a former paper, and as a result of further study, it includes two revised values. New samples of anhydrous magnesium perchlorate, or Anhydrone, silica gel, and alumina were obtained and tested for dehydrating efficiency. The method used was similar to that described in the earlier paper, except that a drying tower replaced the U-tube and each desiccant was tested separately. No change of efficiency value was obtained with anhydrous magnesium percholorate, but new values for silica gel and alumina were found and replace the values originally given.

Following the publication of an earlier paper,[1] claims were made that certain of the desiccants that were tested were not truly representative.

Upon investigation, it was decided that three desiccants should be retested, namely silica gel, activated alumina, and anhydrous magnesium perchlorate. The procedure of testing the desiccants was similar to that originally used, except that a drying tower was substituted for a U-tube. The drying tower was 300 mm in height and was provided with inlet and outlet tubulatures and a ground-glass stopper for closing the top.

The silica gel used in the first tests was a commercial product passing a No. 60 United States Sieve and retained on a No. 200. It was activated by heating in the U-tube at 110° to 130° C, in vacuum, for 5 hours.

The gel used in these tests was furnished by the Davison Chemical Corporation, Baltimore, Md., and was marked 6956–160 (6–16 mesh). It was prepared for use in two tests by heating in the drying tower at 175° to 190° C for 4 hours while passing through it air dried by phosphorus pentoxide. In the remainder of the tests the silica gel was heated in an open vessel at 170° to 190° C for 4 hours and then quickly transferred to the drying tower, which previously had been heated at 105° C for several hours. The tower was immediately closed with the glass stopper; the other outlet was open to a phosphorus pentozide tube. When cool, the lower outlet was closed, and the tower was installed in the constant-temperature cabinet.

The alumina used in the first tests was a commercial product known as Hydralo. It was activated by heating in the U-tube at 150° to

[1] BS J. Research **12**, 241(1934) RP649.

180° C for 6 hours while passing through it air dried by phosphorus pentoxide.

The alumina used in the last tests was furnished by the Aluminum Ore Co., East St. Louis, Ill., through the cooperation of R. B. Derr, of the Aluminum Company of America, Pittsburgh, Pa., and was marked Grade A (8–14 mesh). The material was activated by heating in an open vessel at 175° to 200° C for 4 hours by the same procedure used with the silica gel.

The anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) was obtained from the chemical storeroom of the National Bureau of Standards and was approved personally by the manufacturer.

The new results obtained with silica gel (0.006 ml of residual water per liter of air) show a higher degree of efficiency than was previously obtained (0.03 mg/liter of air).

Similarly, the new results obtained with activated alumina (0.001 mg of residual water per liter of air) show higher efficiency than was indicated by the original tests (0.005 mg/liter of air).

In the case of the anhydrous magnesium perchlorate the new results duplicated the old results (0.002 mg/liter of air).

Apparently, the silica gel and the activated alumina used in the original tests were not representative of products most efficient as drying agents.

However, attention is called to the fact that for adsorption drying agents, it is quite natural to find varying degrees of drying efficiency with different lots of the same agent, depending on details of manufacture and subsequent treatment.

The new values are incorporated in table 1.

TABLE 1.—*Comparative efficiencies of various dehydrating agents*

Number of tests	Material	Volume of air per hour per milliliter of desiccant	Total volume of air per milliliter of desiccant	Residual water per liter of air	Values from published data [a]
		ml	*Liters*	*mg*	*mg/liter*
5	$CuSO_4$ (anhydrous)	36 to 50	0.45 to 0.7	2.8 (2.7 to 2.9)	1.7 at 30° C (7).
4	$CaCl_2$ (granular)	66 to 165	6.1 to 24.2	1.5 (1.4 to 1.6)	
3	$CaCl_2$ (tech. anhy.)	115 to 150	4.0 to 5.8	1.25 (1.23 to 1.27)	
6	$ZnCl_2$ (sticks)	120 to 335	0.8 to 2.1	0.98 (0.94 to 1.02)	0.95 at 30° C (4).
2	$Ba(ClO_4)_2$ (anhydrous).	26 to 36	2.3 to 3.7	0.82 (0.76 to 0.88)	0.29 at 27° C (19).
4	NaOH (sticks)	75 to 170	2.3 to 8.9	0.80 (0.78 to 0.83)	0.16 at 25° C (2).
3	$CaCl_2$ (anhydrous)	75 to 240	1.2 to 7.8	0.36 (0.33 to 0.38)	0.36 at 25° C (3).
3	$Mg(ClO_4)_2.3H_2O$	65 to 160	4.0 to 7.2	0.031 (0.028 to 0.033)	(20).
3	KOH (sticks)	55 to 65	3.2 to 7.2	0.014 (0.010 to 0.017)	0.002 at 25° C (2).
7	Silica gel	43 to 59	2.1 to 5.2	0.006 (0.002 to 0.01) [b]	
4	$CaSO_4$ (anhydrous)	75 to 150	1.2 to 18.5	0.005 (0.004 to 0.006)	0.005 at 25° C (10).
4	CaO	60 to 90	7.6 to 10.1	0.003 (0.003 to 0.004)	0.2 to 0.3 at 25° C (7).
4	$Mg(ClO_4)_2$ (anhydrous).	43 to 53	2.8 to 5.9	0.002 (0.0016 to 0.0024)	(20).
3	Al_2O_3	36 to 63	5.6 to 6.2	0.001 (0.0008 to 0.0012) [b]	0.003 at 25° C (7).
2	BaO	64 to 66	10.6 to 25	0.00065 (0.0006 to 0.0008)	less than 0.0003 at "ordinary temperature" (5).

[a] See literature references cited in the earlier paper.
[b] Revised values.

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STRESS-CORROSION TESTS OF BRIDGE-CABLE WIRE

By Rolla E. Pollard

ABSTRACT

Stress-corrosion cracks were produced in several statically stressed specimens of cold-drawn wire from the Portsmouth Bridge and in one specimen of heat-treated wire from the Mt. Hope Bridge by immersion in dilute nitrate solutions. No cracks were produced in the cold-drawn Mt. Hope replacement wire after long exposure. No cracks were produced by immersing similar specimens in more corrosive media such as distilled water or dilute ammonium sulfate or in inhibitive solutions such as dilute ammonium nitrate or dilute sodium hydroxide. The results conform, in this respect, to the selective corrosion theory of intercrystalline attack. However, due to the limited amount of materials and their incompletely known history, the effect of such factors as composition, fabrication and heat treatment of the steel could not be determined.

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I. INTRODUCTION

The National Bureau of Standards received in August 1940 a number of samples of bridge wire taken from the cables of the General U. S. Grant Suspension Bridge over the Ohio River at Portsmouth, Ohio. These cables were 7⅛ in. in diameter under the wrapping, and each was made up of 1,458 ungalvanized wires of No. 8 gage in three parallel-wire strands. The choice of ungalvanized wire was based on the previous satisfactory performance of similar wires in other bridges over periods of 20 to 50 years' service [1] [1].

After about 12 years of service a number of breaks were discovered in the Portsmouth bridge cables, most of them at the anchorage shoes, and they were replaced by cables made up of galvanized wire. [2]

Some of the broken and unbroken wires from the old cables had previously been subjected to tensile tests and microscopic examination at the Carnegie Institute of Technology. [3] In this report it was concluded that "on the basis of these tests on samples submitted . . . the wire, where not corroded should be satisfactory for this service."

"Of the corroded specimens examined, only those at the anchorage shoes seem dangerously brittle. At these locations, the wire appears

[1] Figures in brackets indicate the literature references at the end of this paper.

to have been subjected to a combination of stress and corrosion, resulting in stress-corrosion cracks. Specimens from other locations, in spite of corrosion, seem as yet to have suffered no important deterioration in mechanical properties; these latter tests have not been extensive."

The purpose of the present investigation was so make tests supplementary to these and, particularly, to attempt to produce experimentally stress-corrosion breaks in the wire similar to those that had occurred in service.

An example of a typical service break is shown in figure 1. The course of most of the fractures was transverse to the axis of the wire for a comparatively short distance and then showed a decided tendency to become diagonal. Figures 2 and 3 show some of the stress-corrosion cracks found near service fractures in the wire, as received. All of the cracks observed occurred in the concave side of the curvature of the wire. This side would be under tension if the wire were straightened out in a cable. The cracks, like the service fractures, were transverse for short distances and then tended to become diagonal.

II. MATERIALS

Twenty samples of the Portsmouth bridge wire, totalling about 86 feet in length, were submitted. The locations of the samples as removed from the cables are given in table 1. The wire was 0.162 in. in diameter, ungalvanized, and had been cold-drawn to a specified minimum tensile strength of 220,000 lb/in^2.

TABLE 1.—*Locations of samples of wire as removed from the cables*

Group number	Location in cables	Number of wires	Approximate length	Remarks
I	*OMU*	2	2 ft. 3 in	Broken at one end.
	OMU	2	1 ft. 9 in	Do.
II	*KBUE*	1	12 ft. 0 in	Broken at both ends.
III	*KBUI*	2	11 ft. 0 in	Do.
		1	8 ft. 0 in	Do.
		3	2 ft. 9 in	Do.
		1	1 ft. 3 in	Do.
		2	0 ft. 9 in	Do.
IV	*KBU*	3	4 ft. 0 in	Broken at one end.
V	*KBDL*	1	4 ft. 0 in	Broken at both ends.
VI	*KBD*	1	5 ft. 0 in	Do.
		1	4 ft. 0 in	Broken at one end.
Totals		20	86 ft. 0 in±	

O, Ohio end; *K*, Kentucky end; *M*, main span; *B*, backstay; *U*, upstream; *D*, downstream; *E*, exterior strand; *I*, interior strand; *L*, lower strand.

The range of composition reported by the Carnegie Institute of Technology is given in table 2. This table also gives the results of analysis of a sample wire of group III, table 1, submitted to the National Bureau of Standards.

Several years ago an investigation of the failure of the heat-treated Mt. Hope Bridge cable wire was made at this Bureau by Swanger and Wohlgemuth [4]. Tests were also made on samples of the cold-drawn wire used to replace the heat-treated wire in the Mt. Hope Bridge cables. Both the original and the replacement wires were hot-dip galvanized. A few samples of both materials were included in the tests, either

stripped or as galvanized, for comparsion with the ungalvanized, cold-drawn Portsmouth Bridge cable wire. The compositions of the Mt. Hope materials are included in table 2.

TABLE 2.—*Composition of materials*

Material	Composition				
	C	Mn	P	S	Si
	%	%	%	%	%
Portsmouth (range of four analyses reported by Carnegie Institute of Technology).	0.69 to 0.84	0.56 to 0.81	0.008 to 0.014	0.031 to 0.037	0.03 to 0.14
Portsmouth (sample from group III, table 1, submitted to National Bureau of Standards).	.83	.53	.008	.029	.14
Mt. Hope, heat-treated (Specification requirements).	.70 to .80	.40 to .60	.04 max	.04 max	.12 to .20
Mt Hope, cold-drawn	.67	.61	.025	.036	.15

All of the samples of the Portsmouth wire, as received, had assumed a curvature which presumably was approximately that to which it had been coiled in the mill. The radius of curvature varied from 10.0 to 12.3 in.

The heat-treated Mt. Hope wire was practically straight, while the radius of curvature of the cold-drawn replacement wire of the Mt. Hope Bridge varied from 23.1 to 24.8 in.

Because of the limited amount of material available, no tensile tests were made. The tensile properties previously reported [3, 4] for the materials are given in table 3.

TABLE 3.—*Tensile properties of materials as reported in references [3] and [4]*

	Tensile strength	Yield strength	Elongation	Reduction of area
	PORTSMOUTH WIRE			
	lb/in.[2]	*lb/in.*[2]	*Percent*	*Percent*
Maximum	265,000	[a] 185,000	[b] 1.7	47.0
Minimum	242,000	167,000	0.5	19.3
	MT. HOPE, HEAT-TREATED-WIRE			
Maximum	237,000	196,200	7.5	53.0
Minimum	201,000	180,100	5.0	9.0
Average	223,000	[c] 189,800	[d] 6.1	37.0
	MT. HOPE, COLD-DRAWN WIRE			
Maximum	226,000	193,300	7.4	42.0
Minimum	216,000	178,200	6.4	33.0
Average	223,000	[c] 182,600	[d] 6.6	40.0

[a] Stress required to produce extension of 0.75 percent.
[b] 10-in. gage length.
[c] Stress required to produce extension of 0.7 percent.
[d] 4-in. gage length.

III. STRESS-CORROSION TESTS

Stressed specimens of the several materials were subjected to corrosion by immersion in distilled water and approximately 0.01 *N* solutions of ammonium nitrate, ammonium nitrite, sodium hydroxide, ammonium sulfate and sodium nitrate. These solutions were selected because of their possible occurrence in the rain or ground waters to which parts of the bridge cables may have been exposed in service. The concentrations used, corresponding to 640 to 850 parts per million, were considerably higher than those usually encountered in rain or in ground waters. It is possible, however, that solutions of comparable concentration could be built up by evaporation of moisture from weaker solutions trapped in anchorage pits or within the cable coverings. The solutions were renewed once a week. During the week the volume of each solution usually was reduced by 10 to 20 percent, depending on the weather. The concentration of the solution, of course, varied inversely as the volume during this time.

Specimens of the several bridge-cable wire materials were statically stressed by changing the curvature of the wire. In most cases the specimens were bent to smaller radii calculated to produce stresses of given magnitudes and held in that position, as illustrated in figure 4. By twisting the loop of small wire around the ends of the bridge wire, the length of the chord could be reduced to the calculated dimension within the accuracy of measurement—about 0.1 in. Specimens of this type are referred to in this report as "bowed" specimens.

The change in extreme fiber stress produced by changing the curvature of the wire was calculated by use of the formula

$$S=Er\ (1/R_2-1/R_1),$$

where

S=maximum change in fiber stress in pounds per square inch;
E=modulus of elasticity (29,000,000 lb/in.^{2});
r=radius of wire, in inches.
R_1=radius of curvature before bending, in inches.
R_2=radius of curvature after bending, in inches.

According to this formula, the Portsmouth wire, which, as received, was curved in coils 20 to 25 in. in diameter, would be subjected to extreme fiber stresses exceeding 200,000 lb/in.^{2} merely by straightening. Accordingly, some specimens of this wire were constrained in a straight position by attaching the ends to a piece of wood, the middle one-third of which had been partially cut away, as illustrated in figure 5. The ends were protected by very heavy coatings of molten tar before immersion in distilled water, the only corrosive media used with this type of specimens (referred to hereafter as "straight" specimens). The tar afforded complete protection to the ends of the specimens, as may be seen in figure 5, which was taken after the completion of the test.

The ends of the bowed specimens were protected by asphalt paint to about 1 in. below the water line during immersion. However, the paint blistered and peeled off rapidly near the water line, and it was necessary to repaint these areas after a few months.

IV. TEST RESULTS

A tabulation of the specimens used, the maximum stresses to which they were subjected, the solutions employed, the exposure period and a brief summary of the test results are given in table 4.

TABLE 4.—*Conditions of stress-corrosion tests of bridge-cable wire*

Specimen designation	Source of bridge-cable wire	Approximate stress	Corrosive medium	Exposure period	Remarks
		*lb/in.*²		*Months*	
1	Portsmouth bridge	146,000	Distilled water	40	Severe corrosive attack, no stress-corrosion cracks, no failures.
2	do	164,000	do	40	Do.
3	do	190,000	do	40	Do.
4	do	196,000	do	40	Do.
[a] H1	Mt. Hope Bridge (heat-treated).	182,000	do	40	Do.
[a] H3	do	178,000	do	40	Do.
[a] H5	Mt. Hope Bridge (cold-drawn).	183,000	do	40	Do.
[a] H7	do	182,000	do	40	Do.
[c] S1	Portsmouth Bridge	216,000	do	40	Do.
[c] S2	do	214,000	do	40	Do.
[c] S3	do	216,000	do	40	Do.
[c] S4	do	210,000	do	40	Do.
5	do	144,000	0.01 *N* NH_4NO_3	8	Cracks, 6 months; failed, 8 months.
6	do	165,000	.01 *N* NH_4NO_3	7	Cracks, 6 months; failed, 7 months.
7	do	185,000	.01 *N* NH_4NO_3	7	Cracks, 6 months; failed, 7 months.
8	do	199,000	.01 *N* NH_4NO_3	6½	Cracks, 6 months; failed, 6½ months.
[a] H2	Mt. Hope Bridge (heat-treated).	183,000	.01 *N* NH_4NO_3	5	Cracks, 3½ months; failed, 5 months.
[a] H6	do	184,000	.01 *N* NH_4NO_3	39½	Severe localized pitting, no cracks, no failure.
9	Portsmouth bridge	144,000	.01 *N* NH_4NO_3	31	Practically no corrosive attack. Discontinued because of difficulty in obtaining and keeping the NH_4NO_3 reagent.
10	do	162,000	.01 *N* NH_4NO_3	31	Do.
11	do	185,000	.01 *N* NH_4NO_3	31	Do.
12	do	206,000	.01 *N* NH_4NO_3	31	Do.
13	do	150,000	.01 *N* NaOH	36	Practically no corrosive attack; no cracks, no failures.
14	do	165,000	.01 *N* NaOH	36	Do.
15	do	181,000	.01 *N* NaOH	36	Do.
16	do	196,000	.01 *N* NaOH	36	Do.
17	do	149,000	.01 *N* $(NH_4)_2SO_4$	31	Remarkably uniform corrosive attack, no cracks, no failures.
18	do	163,000	.01 *N* $(NH_4)_2SO_4$	31	Do.
19	do	186,000	.01 *N* $(NH_4)_2SO_4$	31	Do.
20	do	201,000	.01 *N* $(NH_4)_2SO_4$	31	Do.
21	do	144,000	.01 *N* $NaNO_3$	9½	Failed at deep pit, no cracks.
22	do	163,000	.01 *N* $NaNO_3$	7	Cracks, 3 months; failed, 7 months.
23	do	182,000	.01 *N* $NaNO_3$	3½	Cracks, 3 months; failed, 3½ months.
24	do	207,000	.01 *N* $NaNO_3$	3½	Cracks, 2½ months; failed, 3½ months.
25	do	140,000	.01 *N* $NaNO_3$	4	Cracks, 3½ months; failed, 4 months.
26	do	120,000	.01 *N* $NaNO_3$	9	Cracks, 3½ months; failed 9 months.
27	do	100,000	.01 *N* $NaNO_3$	13	Failed at deep pit, cracks also.
28	do	134,000	.01 *N* NH_4NO_3	5	Cracks, 3½ months; failed, 5 months.
29	do	112,000	.01 *N* NH_4NO_3	4	Cracks, 3½ months; failed, 4 months.
30	do	90,000	.01 *N* NH_4NO_3	19	Unbroken after 19 months.

[a] Stripped.
[b] Hot-dip galvanized.
[c] Straight specimens—all others were bowed.

Further details of the corrosion test results are given below:

Distilled water.—Samples of all the materials were exposed in distilled water. In bowed specimens of Portsmouth wire the stresses ranged from 146,000 to 196,000 lb/in^2. No stress-corrosion cracks or failures occurred in these specimens, although after immersion for 40 months, corrosive attack was very severe (fig. 6). The attack was of a localized nature in that rather large irregular areas were corroded more severely than some corresponding adjacent areas. The edges of these areas were very sharply defined, and within them the corroded surfaces were comparatively smooth. In some of these localized areas near the water line the diameter of the wire was reduced nearly 50 percent, that is, to 0.083 in. from the original diameter of 0.162 in.

The same type of corrosion occurred on the "straight" specimens of Portsmouth wire (fig. 7), on samples of Mt. Hope heat-treated wire (fig. 8), and on Mt. Hope cold-drawn wire (fig. 9) exposed in the bare state. Both the heat-treated and cold-drawn Mt. Hope wires exposed in the hot-dip galvanized condition showed localized pitting after 40 months (figs. 8 and 9).

No stress-corrosion cracks or failures occurred in any of the specimens exposed in distilled water.

Ammonium sulfate.—Bowed specimens of Portsmouth wire immersed in 0.01 *N* ammonium sulfate for 31 months were very severely attacked particularly near the water line, as may be seen in figure 10. In some places the diameter of the wire was reduced 63 percent, from 0.162 to 0.060 in. The corrosive attack was remarkably uniform, and the corroded surface was very smooth except near the water line, where slight irregularities occurred. There were no stress-corrosion cracks or failures.

Ammonium nitrite and sodium hydroxide.—Bowed specimens of Portsmouth wire were exposed in 0.01 *N* solutions of ammonium nitrite and sodium hydroxide under stresses ranging from 144,000 to 206,000 lb/in^2. Both solutions proved to be very good inhibitors in the concentrations used. The specimens showed practically no evidence of corrosion after exposure of 31 months in the nitrite and 36 months in the hydroxide (figs. 11 and 12).

Nitrate solutions.—Of the 14 bowed Portsmouth wire specimens immersed in the 0.01 *N* solutions of ammonium nitrate and sodium nitrate, 11 developed stress-corrosion cracks and failed, apparently as a direct result of such cracking after exposures ranging from 3½ to 9½ months. The appearance of such cracks before the final failure is shown in figure 13. Examples of typical stress-corrosion failures are shown in figures 14 and 15. Longitudinal sections containing stress-corrosion cracks located near the fractures are shown in figures 16 and 17 and at higher magnification in figures 18 and 19.

As may be seen by comparison of these figures with figures 1, 2, and 3, the cracks and fractures produced in these solutions were similar to those which occurred in service. In most cases the course of both cracks and fractures was transverse for a short distance and then became diagonal. Many of the cracks branched longitudinally in two directions. Most of the cracks were quite wide at the top and were filled with corrosion product. It was not readily apparent, therefore, whether they were transcrystalline or intercrystalline in these regions. In the innermost narrower parts, however, particularly after they had assumed a diagonal course, they were definitely intercrystalline in nature, as shown in figure 20.

In most cases the cracks produced in the laboratory tests were located on the convex side of the bowed specimens, as would be expected since this side was in tension. In two instances, however, cracks were also found on the concave, or compression, side of the bowed specimens. One of these cracks is shown in figure 21. It is possible that these cracks had already occurred in service when this part of the wire was in tension and were present in the wire as received.

Two of the 14 bowed specimens immersed in the nitrate solutions failed at exceptionally deep pits on the compression side of the wire. One of these failures is shown in figure 22. Other parts of the same wire showed no evidence of severe pitting. A section through the pit is shown in figure 23. This specimen also contained stress-corrosion cracks on the tension side near the pit, as shown in figure 24. The pit evidently developed faster than the cracks, however, and the final failure occurred at the pit. No stress-corrosion cracks were found on the other specimen that failed at a similar pit.

Only 1 of the 14 bowed specimens of Portsmouth wire exposed in the nitrate solutions did not fail, either by stress-corrosion or because of exceptionally severe localized pitting. This specimen, under a static stress of 90,000 lb/in.^{2}, the lowest used, was immersed for 19 months in 0.01 *N* ammonium nitrate solution without failure. At the end of this period the specimen showed little evidence of corrosive attack in the central portion and only slight localized pitting near the water line (fig. 25).

One bowed specimen of the Mt. Hope heat-treated wire (stripped) and a similar one of the cold-drawn replacement wire (also stripped) were tested in the 0.01 *N* ammonium nitrate solution. The cold-drawn wire did not fail after 39½ months' exposure. Severe localized pitting developed near the water line, but very little corrosive attack occurred in the central portion, and there was no evidence of stress-corrosion cracks. The heat-treated wire, on the other hand, developed numerous stress-corrosion cracks after 3½ months and failed after 5 months' exposure. This fracture was transverse all the way across the wire as shown in figure 26. Longitudinal sections through some of the cracks near the fracture are shown in figures 27, 28, and 29. The intercrystalline course of one of the cracks, particularly in its innermost part, is clearly revealed in these figures.

V. DISCUSSION OF RESULTS

The results of the laboratory tests strongly support the tentative conclusion expressed in the report of the Carnegie Institute of Technology, that the service failures of the Portsmouth Bridge wires were due to the combined effects of stress and corrosion. The possibility of parts of the cables having been exposed to the attack of nitrate solutions of concentrations comparable to those used in the laboratory tests has been pointed out, and the results of these tests show that failures can be caused by the corrosive action of such solutions in combination with imposed stresses much lower than would be produced merely by straightening the wire.

Intercrystalline cracks may be developed in many metals and alloys under certain corrosive conditions or under the combined effects of stress and corrosion. Some metals such as certain aluminum alloys and stainless steel may be subject to intercrystalline corrosion without

the application of stress. On carbon steels the intercrystalline type of corrosive attack usually is produced only when the material is subjected to stress, either imposed or residual. Smialowski [5] has recently reported, however, that intercrystalline penetration was obtained in the absence of mechanical stress in a coarse-grained soft iron which had been stress-relieved at 850° C. After 8 hours in a boiling 50-percent solution of ammonium nitrate, it became so brittle that it disintegrated into individual grains when bent.

Many reports have appeared in the literature on investigations of the intercrystalline cracking of boiler plate and also on the occurrence of similar failures in evaporators and other steel structures subjected under stress to the corrosive action of hot, concentrated nitrate solutions.

Many investigators consider the "caustic embrittlement" of steam boilers to be caused by stress-corrosion. Zappfe [6], however, believes that such embrittlement is due to hydrogen. Whether or not stress-corrosion is involved in the actual service failures of boilers, the production in the laboratory of intercrystalline stress-corrosion cracks in boiler plate steel has been reported many times. The results of some of the most recent investigations indicate that the occurrence of such cracks is influenced by three principal factors: (1) the composition and corrosive action of the corrosive medium; (2) the presence of stress, either imposed or residual; and (3) the composition and structural condition of the steel.

Schroeder and his coworkers [7, 8, 9, 10, 11] produced intercrystalline cracks in statically stressed low-carbon steels in concentrated caustic solutions, particularly those containing small additions of certain oxidizing agents, such as sodium nitrate, potassium permanganate, sodium chromate, lead oxide, and sodium silicate. They advanced the theory that these cracks were produced by the selective corrosive attack of certain solutions which passivate the crystal faces but attack the grain boundaries. They postulate that the atoms at the grain boundaries are acted upon by atomic forces different on one side from those on the other because of the difference in orientation. These atoms, therefore, may be in a strained condition, which is increased when the metal as a whole is under stress. This may cause these atoms to be more easily removed than those in the body of the crystal. If the action of the corrosive medium is too severe, the overall attack obscures the selective action. Severe intercrystalline corrosion occurs when the passivating action of the solution is sufficient to protect the crystal face but not the grain boundaries.

Houdremont, Bennek, and Wentrup [12] tested statically stressed low-carbon steels of various compositions in hot, concentrated solutions containing 30 to 60 percent of calcium nitrate and 3 to 6 percent of ammonium nitrate. From their results they concluded that the production of intercrystalline cracks is strongly influenced by a critical structural condition of the steel, which depends not only on its composition but also on its previous treatment, particularly heating or annealing. They found that susceptibility to intercrystalline cracking decreased with higher carbon and aluminum contents and that completely deoxidized steels had high resistance, whereas steels heated in an atmosphere of nitrogen had low resistance to this type of attack.

It should be pointed out that most of the investigations cited above

were concerned primarily with the effect of hot, concentrated caustic or nitrate solutions on stressed low-carbon steels, such as would be suitable for boiler plate. Most of the investigators reported no intercrystalline cracking in solutions containing less than 25 to 30 percent of nitrates—usually sodium, ammonium or calcium nitrates or mixtures of these salts.

Very little information is available in the literature concerning the production of intercrystalline cracks in high-carbon steels or by dilute solutions comparable to those used in the present investigation. Schroeder and Berk [11] obtained intercrystalline cracks in statically stressed steel specimens by selective electrolytic corrosive action. The specimens were made anodes in solutions containing as little as a few parts per million of sodium chloride or sodium nitrate. When the current was properly adjusted the only evidence of general corrosion was darkening of the surface, but the specimens were deeply cracked or broken in a few days. They also obtained intercrystalline cracks in stressed steel specimens immersed for a few days in dilute nitric acid solutions containing manganous chloride. They considered that the action of the manganous chloride probably was to catalyze the decomposition of the nitric acid, thus aiding the selective attack.

The results of the present investigation are in line with the selective corrosion theory of intercrystalline attack. No intercrystalline cracks were produced either in the severely corrosive media, distilled water and sodium sulfate or in the completely inhibitive solutions sodium hydroxide and sodium nitrite. In the nitrate solutions the general attack was very slight, but intercrystalline cracks, and occasionally unusually severe and extremely localized pits, were produced. A marked difference was noted in the character of the corrosion products produced in the different solutions, which may have some bearing on the nature of the corrosive attack. In the severely corrosive media large amounts of loose, nonadherent rust was formed, which was easily removed by running tap water or by wiping with a damp cloth. In the nitrate solutions a thin, tightly adherent coating of rust was quickly formed, after which the general corrosive attack, as measured by the further appearance of rust, proceeded very slowly. In the completely inhibitive solutions, very little rust was formed.

Because of the limited amount of material available, it was not possible to determine definitely whether or not there is a lower limit of imposed static stress below which failure of the bridge-wire samples would not occur. At stresses in the neighborhood of the yield strength some of the results were rather erratic, but at lower stresses the time of exposure necessary to cause failure seemed to increase considerably. The lowest stress at which stress-corrosion cracks were obtained within a reasonable length of time was 100,000 lb/in^2. It is possible, however, that exposure for longer periods, comparable to those which might occur in service, would cause failure at lower stresses.

It should be pointed out that the stresses discussed above are the nominal static stresses imposed by bending the wire. Because of the difficulty in evaluating the residual stress in a curved wire of small diameter, its possible presence was not taken into account, and therefore the imposed stress may not be the true stress. Cold-drawing operations usually result in residual stresses whose distribution is such

that the surface of the drawn wire is in tension. As the Portsmouth wire was not heated after drawing, it is probable that the convex side of the bowed specimens of this material were under some residual tensional stress in addition to the applied stress. In these cases the actual stress, therefore, might be considerably higher than the nominal applied stress. The surface of heat-treated wires might be either in tension or compression, depending on the rate of cooling. As the heat-treated Mt. Hope wire was both tempered and hot-dip galvanized, it would be expected that any residual stress resulting from quenching would be largely relieved. Similarly, hot-dip galvanizing would act as a stress-relieving treatment for the cold-drawn Mt. Hope wire. In these cases it is probable, therefore, that the applied stress was very nearly the true stress.

The same concentration of solution 0.01 *N*, was used in all the tests. The possible effect of variation in solution concentration on the combined effect of stress and corrosion, therefore, was not determined. Further study of the effect of other corrosive media, particularly dilute sodium chloride solutions, such as might be encountered in marine exposures, would seem to be desirable.

Very little information can be gleaned from the results of the present investigation in regard to the effect of the composition and structural condition of the steel on the formation of stress-corrosion cracks. It is true that of three wire materials of very similar composition, one cold-drawn and one heat-treated developed cracks, whereas the other cold-drawn material did not. However, because of the limited number of specimens, particularly of the two materials last-named, no definite deductions are justified.

It is evident from a comparison of figures 28 to 33, inclusive, that the microstructures of the materials do not reveal the effect of any differences in composition, fabrication, or heat treatment to which their differences in corrosion behavior could be attributed. Further investigation under better controlled conditions would be necessary to determine the effect of these variables.

VI. SUMMARY

Static stress-corrosion tests were made on samples of cold-drawn Portsmouth Bridge cable wire and on a few samples of heat-treated Mt. Hope Bridge cable wire and the cold-drawn wire used in the replacement cables of the Mt. Hope Bridge.

Stress-corrosion cracks and failures were produced in nearly all the samples of Portsmouth wire and in one sample of heat-treated Mt. Hope wire by immersion in 0.01 *N* solutions of ammonium or sodium nitrate.

The production of these cracks in the laboratory under conditions similar to those which might have existed in service confirms the previous tentative conclusion that service failures of the Portsmouth Bridge wires were due to stress corrosion, and demonstrates the possible manner of their formation.

Stress-corrosion cracks were not produced in more corrosive solutions, such as distilled water or ammonium sulfate, nor in completely inhibitive solutions, such as ammonium nitrite or sodium hydroxide (all solutions 0.01 *N*). The lowest value of imposed stress under which stress-corrosion cracks were found in the Portsmouth wire was

100,000 lb/in². No account was taken, however, of the possible presence of residual stress, and the imposed stress probably was not the true stress.

No stress-corrosion cracks were produced in a statically stressed specimen of cold-drawn Mt. Hope replacement wire exposed in one of the nitrate solutions, although this material was similar in composition and physical properties to the Portsmouth wire.

A more complete study of stress-corrosion cracking in dilute solutions would seem to be desirable, particularly if carried out under conditions where variables such as residual stress could be controlled and the effect of such factors as composition, fabrication, and heat treatment of the steel determined.

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WASHINGTON, June 12, 1944.

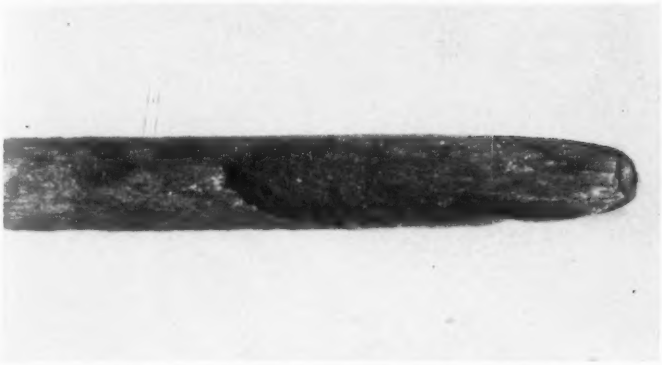

FIGURE 1.—*Example of service fracture of Portsmouth bridge wire, as received.*
Broken end of wire from group III, table 2: ×3.

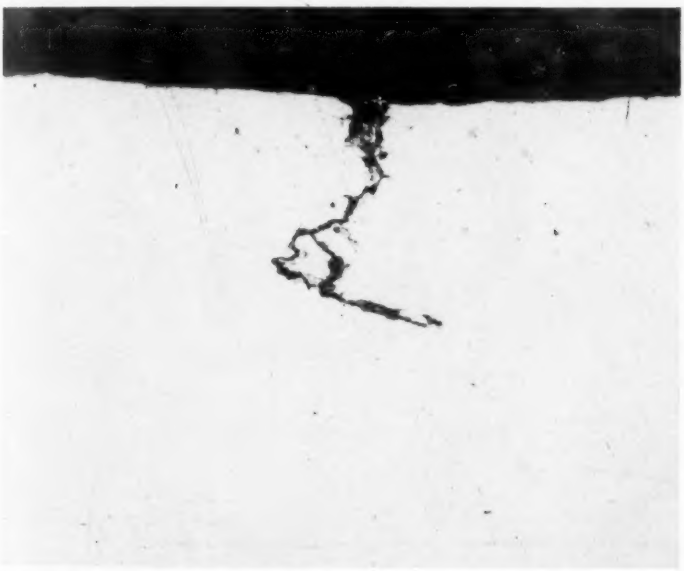

FIGURE 2.—*Stress-corrosion crack near service fracture of Portsmouth bridge wire.*
Longitudinal section, as received. Unetched; ×100.

FIGURE 3.—*Stress-corrosion cracks near fracture of Portsmouth bridge wire.*
Longitudinal section, as received. Unetched; ×100.

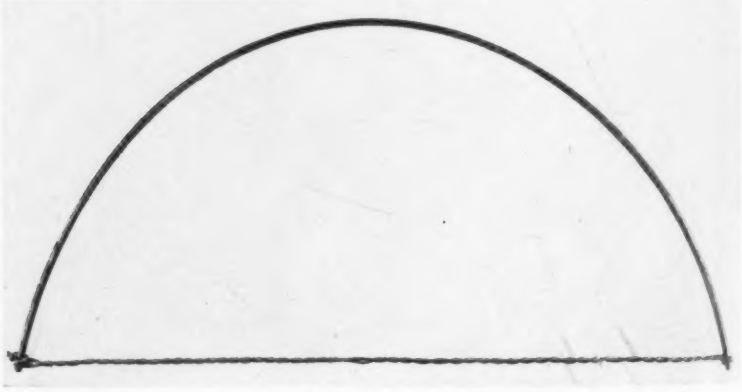

FIGURE 4.—*Example of "bowed" bridge wire specimens tested under static stress in various corrosive media;* ×1/4.

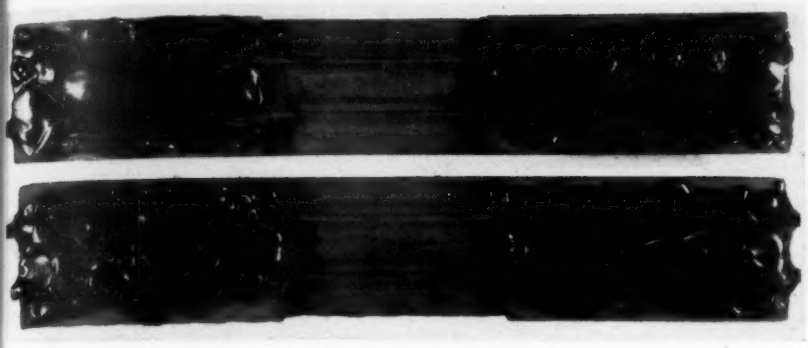

FIGURE 5.—*Example of "straight" specimens of bridge wire tested under static stress, in distilled water;* $\times 1/4$.

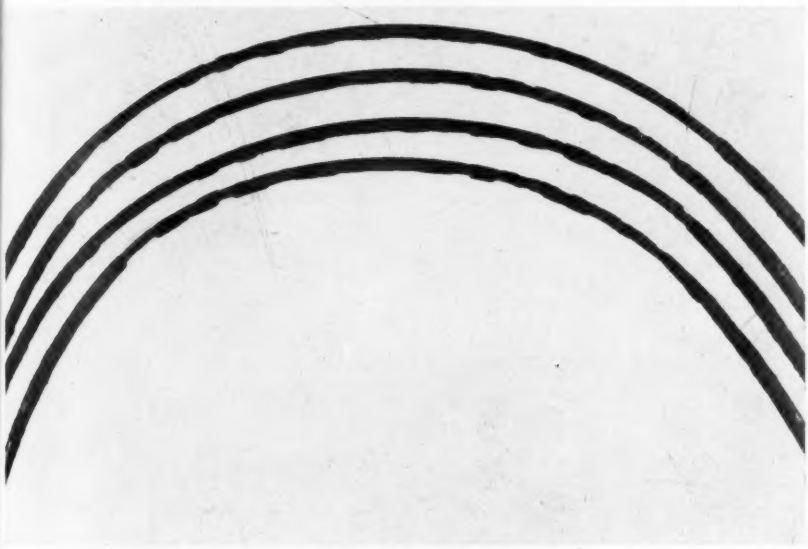

FIGURE 6.—*"Bowed" specimen of Portsmouth bridge wire after immersion for 40 months in distilled water.*

Note the severe, nonuniform corrosive attack. The specimens were designated 1, 2, 3, and 4 from top to bottom; $\times 1/2$.

FIGURE 7.—*"Straight" specimens of Portsmouth bridge wire after immersion for 40 months in distilled water.*

The corrosive attack was severe and nonuniform. The specimens were designated S1, S2, S3, and S4 from top to bottom; ×1.

FIGURE 8.—*"Bowed" specimens of heat-treated Mt. Hope bridge wire after immersion for 40 months in distilled water.*

Note the severe, nonuniform, corrosive attack. Specimen 3, top, was hot-dip galvanized. Specimen No. 1, bottom, was stripped; ×1/2.

FIGURE 9.—*"Bowed" specimens of cold-drawn Mt. Hope bridge wire after immersion for 40 months in distilled water.*

Note the severe, nonuniform corrosive attack. Specimen 7, top, was hot-dip galvanized. Specimen 5, bottom, was stripped; ×1/2.

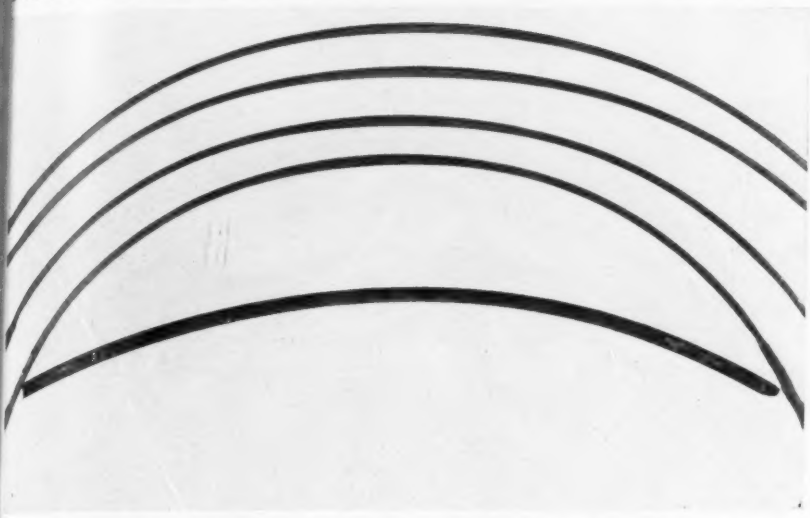

FIGURE 10.—*"Bowed" specimens (Nos. 17, 18, 19, 20, top to bottom) of Portsmouth bridge wire after immersion for 31 months in a 0.01 N solution of ammonium sulfate.*

The corrosive attack was severe but very uniform. A sample of the wire as received is shown below to demonstrate the reduction in diameter due to corrosion; ×1/2.

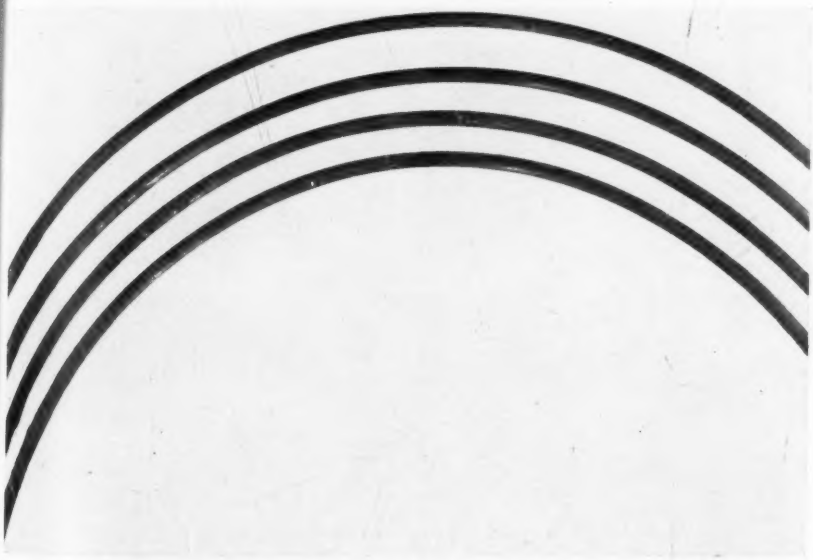

FIGURE 11.—*"Bowed" specimens (Nos. 9, 10, 11, 12, top to bottom) of Portsmouth bridge wire after immersion for 31 months in a 0.01 N solution of ammonium nitrites.*

The solution was almost completely inhibitive and the samples show no evidence of corrosive attack; ×1/2

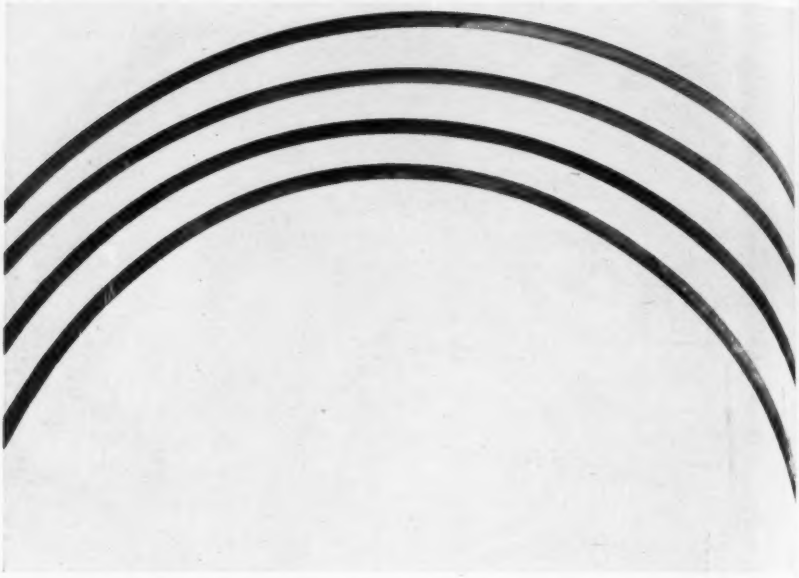

FIGURE 12.—*"Bowed" specimens (Nos. 13, 14, 15, 16, top to bottom) of Portsmouth bridge wire after 36 months' immersion in a 0.01 N solution of sodium hydroxides.*

The samples show no evidence of corrosive attack; ×1/2.

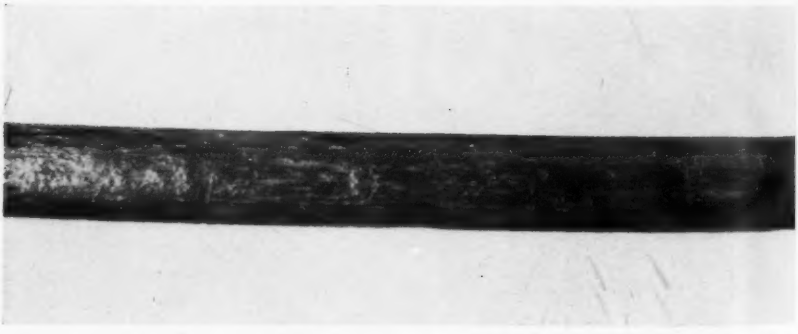

FIGURE 13.—*Appearance of stress-corrosion cracks in a "bowed" specimen (No. 8) of Portsmouth bridge wire prior to failure.*

The cracks appeared after 6 months of immersion, under static stress, in a 0.01 *N* solution of ammonium nitrate; ×3.

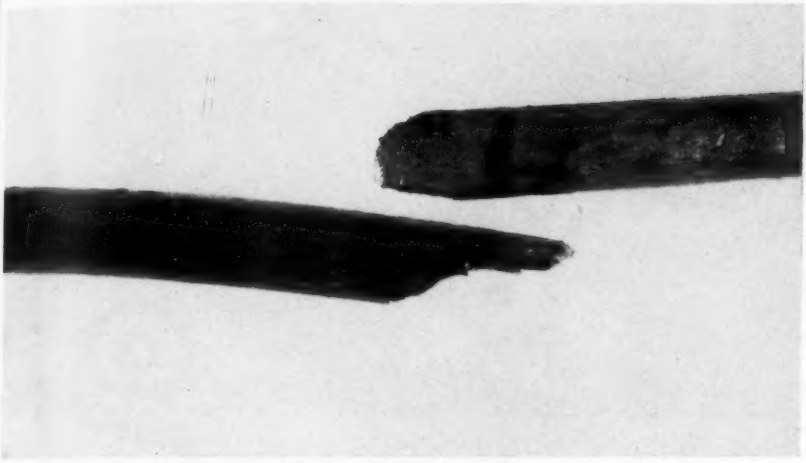

FIGURE 14.—*Appearance of stress-corrosion fracture of "bowed" specimen 8 shown in figure 13 after 6½ months immersion; ×3.*

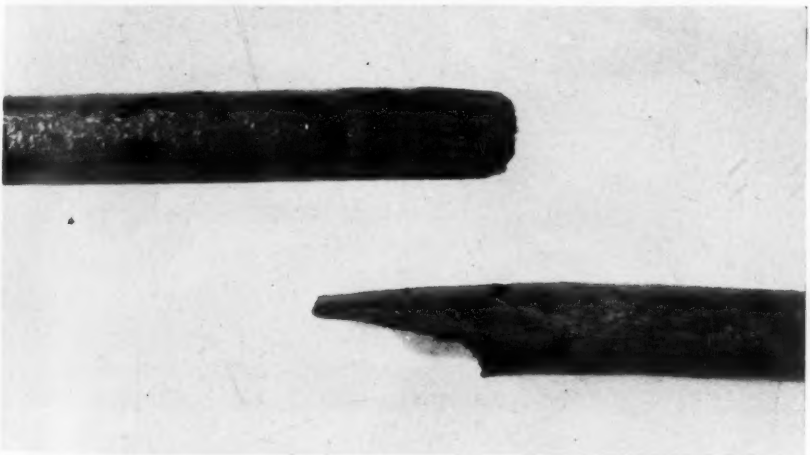

FIGURE 15.—*Stress-corrosion fracture of "bowed" specimen 22 of Portsmouth bridge wire after immersion for 7 months in a 0.01 N solution of sodium nitrate; ×3.*

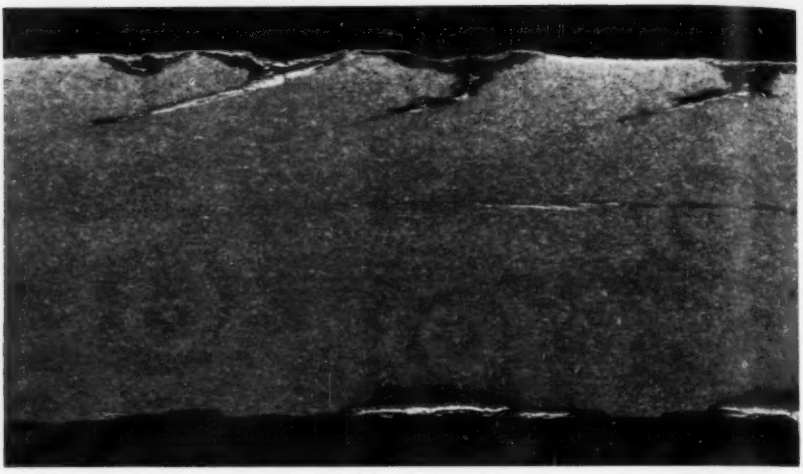

FIGURE 16.—*Longitudinal section showing cracks near the stress-corrosion fracture of "bowed" specimen 7 of Portsmouth bridge wire immersed 7 months in a 0.01 N solution of ammonium nitrate.*

Nital etching; ×12.

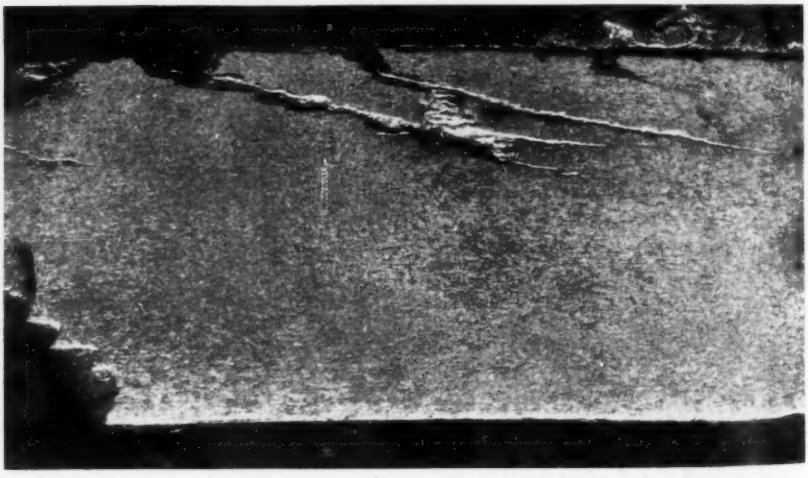

FIGURE 17.—*Longitudinal section showing crack near the stress-corrosion fracture of "bowed" specimen 22 of Portsmouth bridge wire immersed 7 months in a 0.01 N solution of sodium nitrate.*

Unetched; ×12.

FIGURE 18.—*One of the cracks of figure 16 at higher magnification.*
Unetched; ×100.

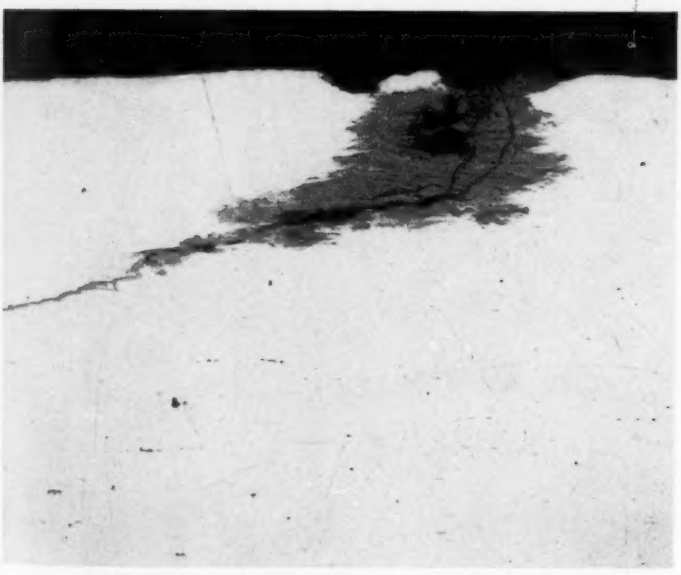

FIGURE 19.—*One of the cracks of figure 17 at higher magnification.*
Unetched; ×100.

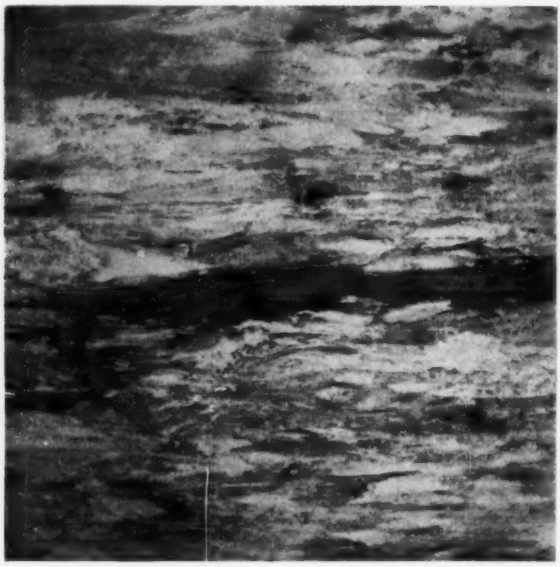

FIGURE 20.—*Lower part of a stress-corrosion crack in a cold-drawn bridge wire (Portsmouth) to show its intercrystalline character in that region.*

Nital etching; ×500.

FIGURE 21.—*Stress-corrosion crack on compression side of "bowed" specimen 29 of Portsmouth wire immersed in a nitrate solution.*

It is probable that this crack occurred in service and was in the material as received. Nital etching; ×100.

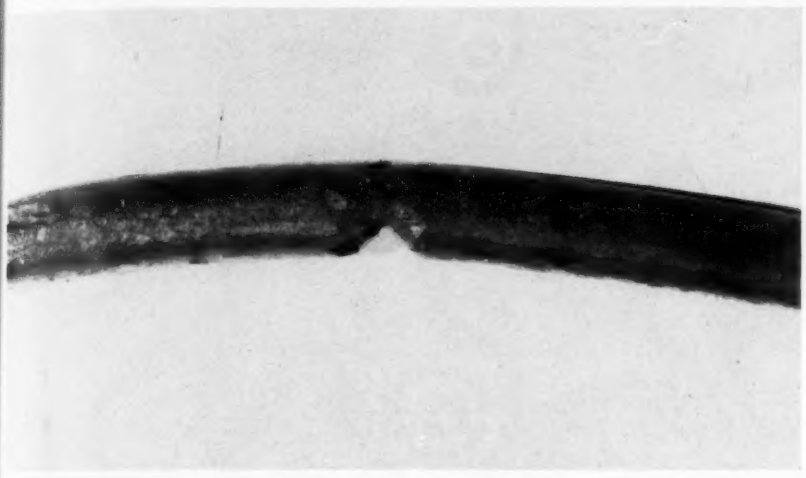

FIGURE 22.—*Failure of "bowed" specimen 27, Portsmouth bridge wire, at a very deep localized pit after immersion, under static stress, in a 0.01 N solution of sodium nitrate for 13 months.*

Aside from the local pit the specimen shows very little evidence of corrosive attack; ×3.

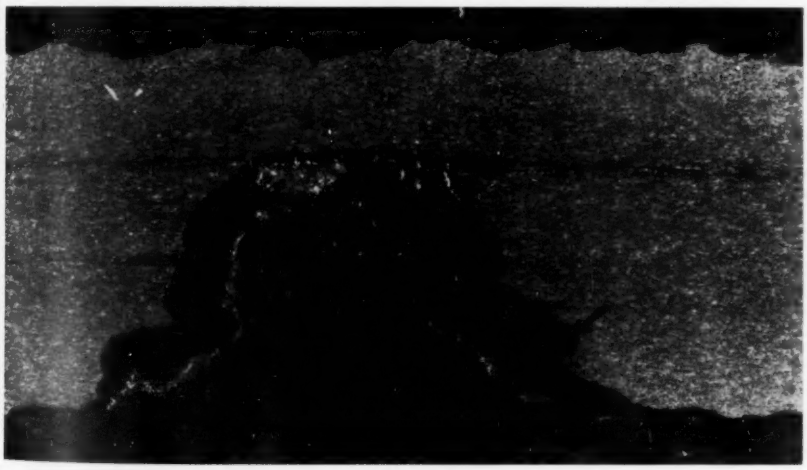

FIGURE 23.—*Longitudinal section through deep pit of figure 22 on compression side of specimen 27, Portsmouth bridge wire.*

Nital etching; ×12.

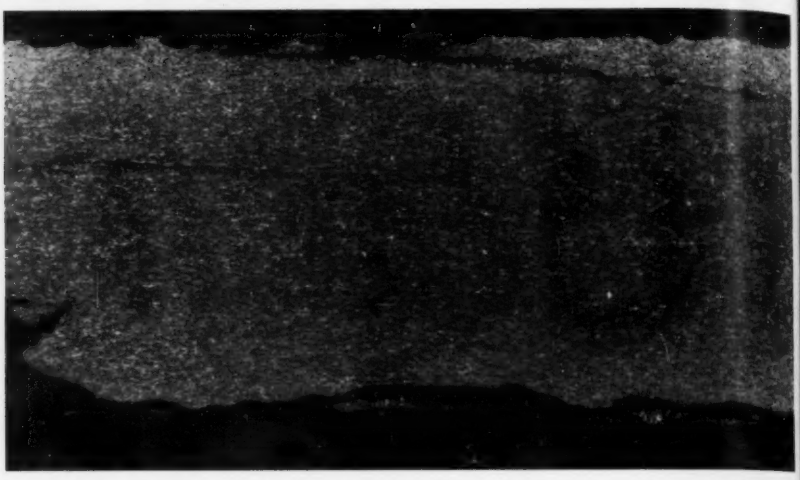

FIGURE 24.—*Stress-corrosion crack on tension side of the same specimen shown in figures 22 and 23.*

The location of the crack with respect to the pit is indicated by the arrow which points out an area common to both figures 23 and 24.

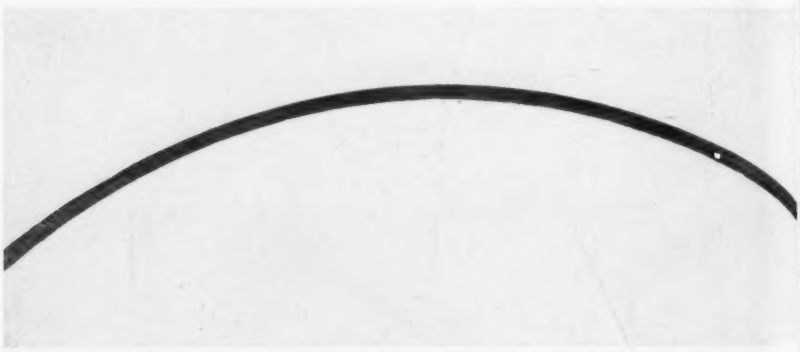

FIGURE 25.—*"Bowed" specimen 30, Portsmouth bridge wire, which did not fail after immersion for 19 months in 0.01 N ammonium nitrate.*

This is the only one of 14 samples of Portsmouth wire which did not fail in stress-corrosion tests in nitrate solutions; ×1/2.

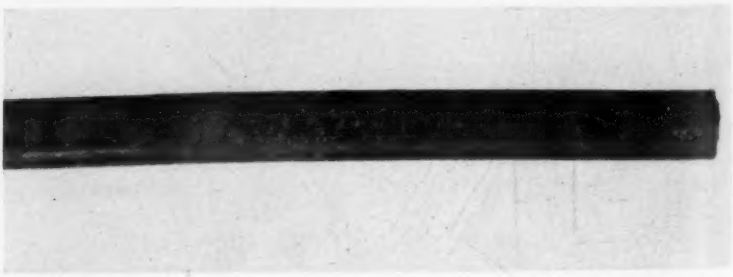

FIGURE 26.—*Stress-corrosion fracture of "bowed" specimen H2, heat-treated Mt. Hope bridge wire immersed 5 months in a 0.01 N solution of ammonium nitrate;* ×2.

FIGURE 27.—*Longitudinal section showing stress-corrosion cracks near the fracture of the specimen of heat-treated Mt. Hope bridge wire shown in figure 26.*

Nital etching; ×12.

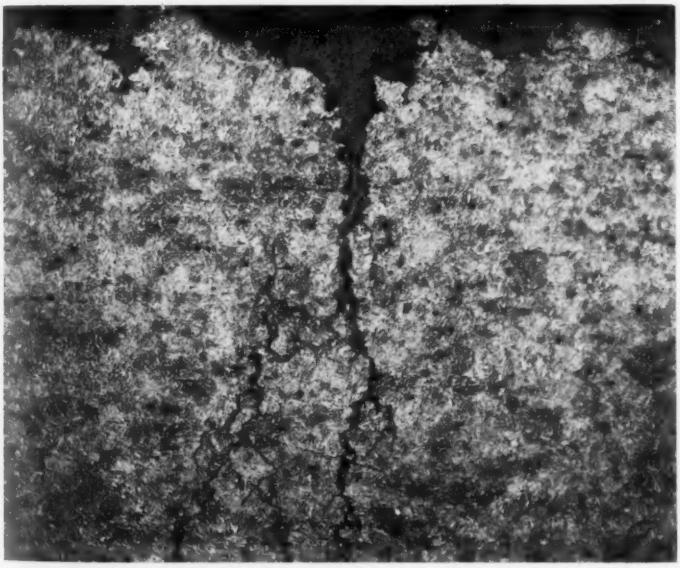

FIGURE 28. *—One of the cracks of figure 27 at higher magnification.*

The crack is intercrystalline over most of its course. Nital etching; ×100.

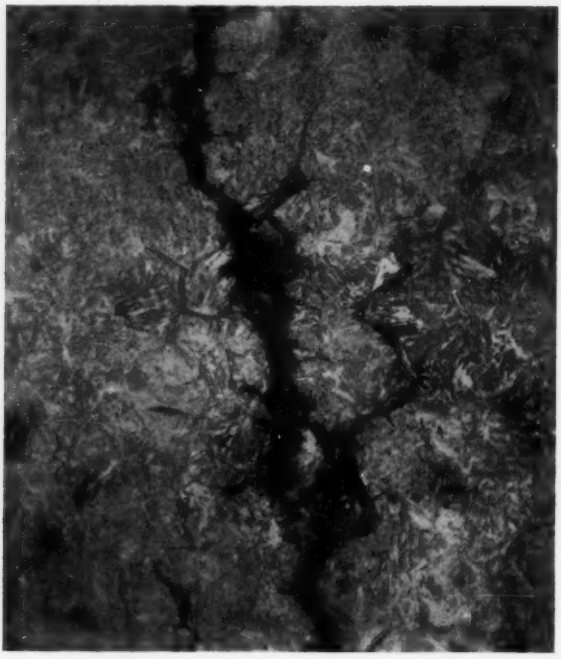

FIGURE 29.—*Part of figure 28 at higher magnification showing the intercrystalline character of the crack and the quenched and tempered structure of the material.*

Nital etching; ×100.

FIGURE 30.—*Microstructure of the cold-drawn Portsmouth wire (specimen No. 25) in a longitudinal section showing a stress-corrosion crack.*

Nital etching; ×100.

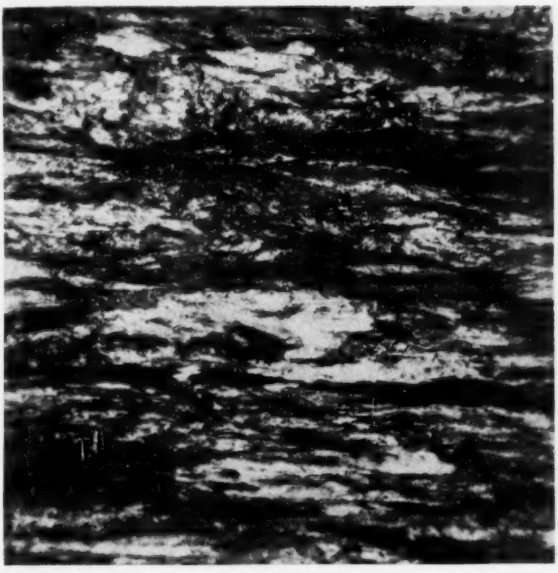

FIGURE 31.—*Microstructure of cold-drawn Portsmouth wire at higher magnification.*

Nital etching; ×500.

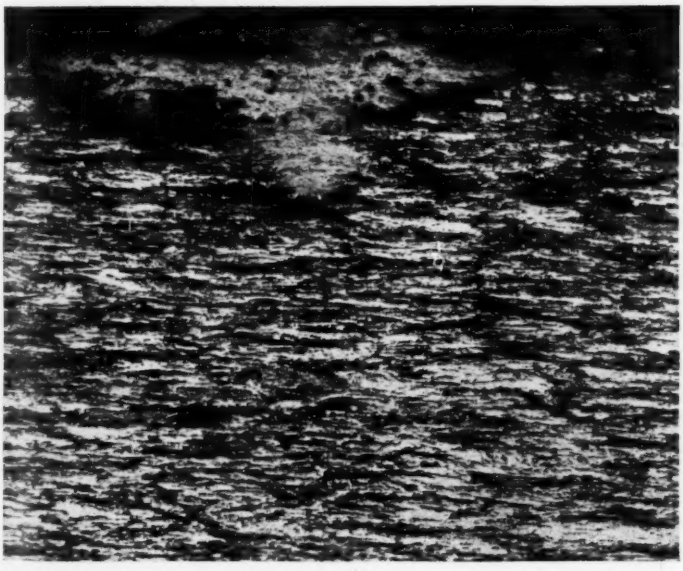

FIGURE 32.—*Microstructure of cold-drawn Mt. Hope replacement wire (specimen H6) in a longitudinal section showing a deep corrosion pit produced by immersion for 40 months in 0.01 N ammonium nitrate.*

Nital etching; ×100.

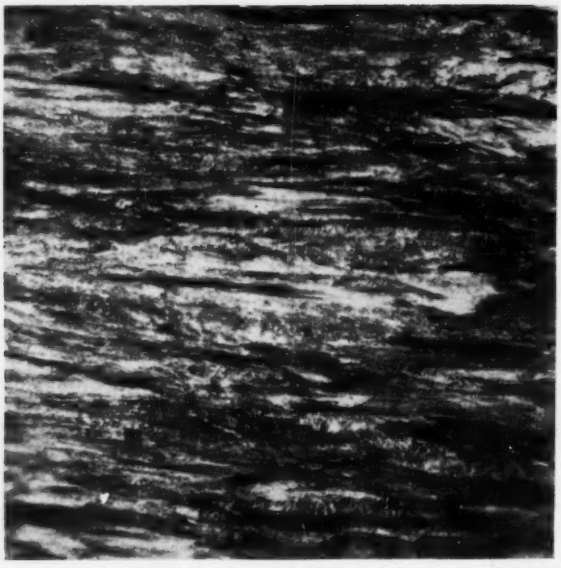

FIGURE 33.—*Microstructure of cold-drown Mt. Hope replacement wire at higher magnification.*

Nital etching; ×500.

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TRASNFORMATIONS OF THE FUNDAMENTAL EQUATIONS OF THERMODYNAMICS

By Floyd Buckley

ABSTRACT

A substitution group for generating families of thermodynamic formulas is derived. The method of derivation is based upon the transformation properties of a "group of functions" under a contact transformation. There exists a characteristic function and a "group of functions" for each representation, that is, each coordinate system, and to each function of the group there is an associated contact transformation which transforms the group into its equivalent in another representation. The invariance of the functional form of the characteristic groups of functions under contact transformations is equivalent to invariance under a substitution group $\mathscr{G}^*$ on the space $(EHFG)(V-S-TP)$. The group $\mathscr{G}^*$is independent of the representation and can be generated geometrically.

There are four contact transformations (including the identity) a sociated with each representation. These transformations are equivalent, and from them families of equations can be found which are invariant under the group $\mathscr{G}^*$. Other families can be found among the transformation formulae for the higher derivatives.

Formulas deducible by simple operations, for example, differentiation, on the characteristic group of functions of a given representation provide basic forms for families invariant under the group $\mathscr{G}^*$. The number of members in a family is 1, 2, 4, or 8.

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I. INTRODUCTION

The existence of symmetry relations between certain sets of thermodynamic formulas has been recognized since the classical work of Gibbs. Nevertheless, Koenig [1] [1] seems to have been the first to exhibit these relations in the compact form of a substitution group on the thermodynamic functions E, H, F, G and the variables of state V, S, P, T; N_i. The method of derivation was not given, although it was shown how the group can be generated from the symmetry properties of a square. The purpose of this article is to present a derivation of Koenig's substitution group by making use of the transformation properties of the fundamental thermodynamic equations. The transformations employed are the Cylindrical Tangential (Contact) Transformations studied by Lie.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. THE FUNDAMENTAL EQUATIONS

The necessary assumptions are those given by Caratheodory [2] in his axiomatic development of the general theory. The following discussion does not require an analysis of these assumptions. Nor does it require a description of the methods used in establishing the relation between the general mathematical structure and experimental thermodynamics, particularly the determination of the characteristic function associated with a selected set of physical and chemical variables. It will suffice to recall that in a given description, that is, with a given choice of variables, there exists a characteristic function Z appropriate to a given physical system, which is the solution of an exact differential equation of the Pfaff type:

$$dZ-\sum_i X_i dX_i=0.$$

Once Z has been found, the general behavior of the system can be conveniently described with the aid of auxiliary functions defined in terms of Z and its partial derivatives. For example, in a reference system (description) using V, S; N_i as independent variables, all general thermodynamic formulas, that is, those formulas independent of an equation of state, are derivable from the characteristic Energy function, E, and the basic equations

$$\begin{aligned} H&\equiv E-V\frac{\partial E}{\partial V}\\ F&\equiv E-S\frac{\partial E}{\partial S} \qquad (1)\\ G&\equiv E-V\frac{\partial E}{\partial V}-S\frac{\partial E}{\partial S}=H+F-E. \end{aligned}$$

The Energy function is a function only of the state of the system and satisfies the conditions:

Equilibrium State	$dE=0$	$\delta V=0$	$\delta S=0$	$\delta N_i=0$.
Reversible Process	$dE=0$	$\delta V=0$	$\delta S=0$	$\delta N_i=0$.
Natural Process	$dE=0$	$\delta V=0$	$\delta S>0$	$\delta N_i=0$.
Unnatural Process	$dE=0$	$\delta V=0$	$\delta S>0$	$\delta N_i=0$.

The functions H, F, G are not uniquely defined, but in practical application the arbitrariness drops out. Legitimate operations on equations 1 generate a collection C, of formulas valid in the description V, S; N_i.

III. THE PROBLEM

Assume a new choice of independent variables V', S' (it will henceforth be assumed that the chemical variables, N_i, remain unchanged), that is, mode of description. On physical grounds, there exists a transformation, $\mathbf{t}$, and its inverse, $\mathbf{t}^{-1}$, such that

$$\begin{aligned} (V,S)&\rightarrow(V'S',)=\mathbf{t}(V,S)\\ (V',S')&\rightarrow(V,S)=\mathbf{t}^{-1}(V',S') \end{aligned}$$

The new variables defined by **t**:

$$V' = f(V,S)$$
$$S' = g(V,S)$$

are functionally independent and are therefore soluble for the old variables as functions of the new.

The functions E, H, F, G, and formulas C will transform into functions of the new coordinates, which will in general take on new functional forms. The two modes of description are completely equivalent and under the transformation, **t**, formulas must transform into identities in the new variables.

Anticipating later results, let it be assumed that under the transformation, **t**, on the physical variables

$$(V',S') = \mathbf{t}(V,S)$$

and the associated transformation, **T**, on the functions E, H, F, G:

$$(E'H'F'G') = \mathbf{T}(EHFG)$$

the form of the fundamental equations remains invariant. Then it is clear that under the combined transformation **Tt** on the complementary sets $(EHFG)$ and (VS), the formulas C also remain invariant. The problem can be formulated as follows: If the basic equations of thermodynamics are written in terms of a particular set of physical variables of state, what transformation on the dependent functions and associated transformation on the independent variables, leave the form of the equations invariant? If it should happen that the combined transformations **Tt** constitute a group **G**, fundamental formulas will remain invariant under **G**. All modes of description associated to **G** are equivalent and the group **G** characterizes a fundamental arbitrariness in the thermodynamic description of all systems.

The problem is analogous to that encountered in the Relativity Theory. It is well known that if the electromanetic field vectors E, H undergo a particular linear transformation and the independent variables $(xyzt)$ undergo an associated linear transformation (the Lorentz-Einstein Transformation), the fundamental equations of the field remain invariant. The arbitrariness of the description (theory) is characterized by the Lorentz-Einstein Group, and all reference frames associated to the group are equivalent.

IV. TANGENTIAL TRANSFORMATIONS

The general Tangential Transformation is defined by Lie [3] as follows:

"When Z, $x_1 \ldots\ldots X_n$, $P_1 \ldots\ldots P_n$ are $2n+1$ independent functions of the $2n+1$ independent quantities z, $x_1 \ldots\ldots x_n$, $p_1 \ldots\ldots p_n$ such that the equation

$$dZ - \sum_{i=1}^{n} P_i dX_i = \rho\left(dz - \sum_{i=1}^{n} p_i dx_i\right)$$

$$\rho \neq 0$$

is identically satisfied, the transformation

$$z'=Z(z,x_i,p_i)$$
$$x_j'=X_i(z,x_i,p_i)$$
$$p_j'=P_i(z,x_i,p_i)$$

is a tangential (contact) transformation."

The test of a given set Z, X_i, P_i is provided by Lie's Theorem [3]:

"The necessary and sufficient conditions that

$$dZ-\sum_{i=1}^{n}P_i dX_i=\rho(dz-\sum_{i=1}^{n}p_i dx_i)$$

be identically satisfied are

$$[ZX_i]=[X_iX_j]=[P_iX_j]=[P_iP_j]=0$$

$$[P_iX_i]=\rho \qquad \rho[ZP_i]=-\rho P_i,$$

provided Z, X_i, P_i are functionally independent, and

$$\rho=\frac{\partial Z}{\partial z}-\sum_{i=1}^{n_1}P_i\frac{\partial X_i}{\partial z}\neq 0.$$

Conversely, $\rho\neq 0$ is sufficient for the functional independence of Z, X_i, P_i."

The bracket symbol is defined by

$$[fg]=\sum_{i=1}^{n_1}\left(\frac{df}{dx_i}\frac{\partial g}{\partial p_i}-\frac{dg}{dx_i}\frac{\partial f}{\partial p_i}\right).$$

The equations which suffice to determine the Z, X_i, P_i, ρ are $2n+1$ in number. Hence there will be an arbitrary element in solution unless some further condition is imposed upon the system. If Z is specified, the X_i, P_i are completely determined. The class of Cylindrical Tangential Transformations is defined by the restriction that the X_i, P_i are independent of z. Application of the conditions of Lie's Theorem then requires that

$$Z=\rho z+\phi(x_i, p_i),$$

where ρ is a constant.

For the case $n=3$, the conditions of Lie's Theorem are not violated if we choose

$$z=f(xy) \qquad p_1=\frac{\partial z}{\partial x}=z_x \qquad p_2=\frac{\partial z}{\partial y}=z_y.$$

Then

$$dz'-p_1'dx'-p_2'dy'\equiv\rho(dz-z_xdx-z_ydy)\equiv 0,$$

and if z' is chosen as a function of z, x, y, z_x, z_y the variables p_1', p_2', x', y' are determined. The transformation insures the exactness of dz', and hence z' plays the same role in the primed coordinates as z does in the unprimed.

V. THE LEGENDRE TRANSFORMATIONS

The thermodynamic transformations between the four equivalent modes of description in the sets of variables (V,S), (P,S), (V,T), (P,T) are related to the three Legendreian Cylindrical Tangential Transformations defined by ($Z_{1x1}=\partial Z_1/\partial x_1$, etc):

$$\begin{aligned} &(a) \quad Z_2=Z_1-Z_{1x_1}x_1 \\ &(b) \quad Z_3=Z_1-Z_{1y_1}y_1 \\ &(c) \quad Z_4=Z_1-Z_{1y_1}y_1=Z_2+Z_3-Z_1. \end{aligned} \tag{1'}$$

Applying the fundamental theorem, it is found that solutions for these cases are

$$\begin{array}{llll} (a) & Z_2=Z_1-Z_{1x_1}x_1 & Z_{2x_2}=x_1 & Z_{2y_2}=Z_{1y_1} \\ & & x_2=-Z_{1x_1} & y_2=y_1 \\ (b) & Z_3=Z_1-Z_{1y_1}y_1 & Z_{3x_3}=Z_{1x_1} & Z_{3y_3}=-y_1 \\ & & x_3=x_1 & y_3=Z_{1y_1} \\ (c) & Z_4=Z_1-Z_{1x_1}x_1-Z_{1y_1}y_1 & Z_{4x_4}=x_1 & Z_{4y_4}=-y_1 \\ & & x_4=-Z_{1x_1} & y_4=Z_{1y_1} \end{array} \quad \rho=1 \tag{2}$$

Under these transformations:

$$\begin{array}{llll} (a) & Z_1=Z_2-Z_{2x_2}x_2 & Z_{1x_1}=-x_2 & Z_{1y_1}=Z_{2y_2} \\ & & x_1=Z_{2x_2} & y_1=y_2 \\ (b) & Z_1=Z_3-Z_{3y_3}y_3 & Z_{1x_1}=Z_{3x_3} & Z_{1y_1}=y_3 \\ & & x_1=x_3 & y_1=-Z_{1y_3} \\ (c) & Z_1=Z_4-Z_{4x_4}x_4-Z_{4y_4}y_4 & Z_{1x_1}=-x_4 & Z_{1y_1}=y_4 \\ & & x_1=Z_{4x_4} & y_1=-Z_{4y_4} \end{array} \quad \rho=1 \tag{3}$$

It is to be observed that:

1. The form of the equation defining the Legendre function is invariant under the transformation.
2. The transformations are involutory, that is, applied twice in succession they generate the identity transformation.
3. The Legendre functions defining the inverse transformations can be obtained by a simple substitution. Thus if:

$$\begin{array}{l} Z_1 \leftrightarrow Z_i \end{array} \qquad \begin{array}{l} (|Z_{1x}|,\ |x_1|) \leftrightarrow (|Z_{ix_i}|,\ |x_i|) \\ (|Z_{1y}|,\ |y_1|) \leftrightarrow (|Z_{iy_i}|,\ |y_i|) \end{array} \quad i=2,3,4.$$

then equations $2 \leftrightarrow 3$.

The absolute values $|x_i|$, $|y_i|$, $|Z_{ix_i}|$, $|Z_{iy_i}|$ must be taken in order to compensate for the change in sign occasioned by transposition when the equations are solved in the usual fashion.

The three simple substitutions carrying equations 2 into 3 can also be considered as linear transformations on complementary sets of quantities. Those on x_1, y_1, Z_{1x_1}, Z_{1y_1}, including the identity, can be conveniently written in matrix form. They are

$$\begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix} = \mathbf{t}_{11} \begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix} \qquad \begin{pmatrix} -x_2 \\ -y_2 \\ Z_{2x_2} \\ Z_{2y_2} \end{pmatrix} = \mathbf{t}_{21} \begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix}$$

$$\begin{pmatrix} x_3 \\ y_3 \\ Z_{3x_3} \\ Z_{3y_3} \end{pmatrix} = \mathbf{t}_{31} \begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix} \qquad \begin{pmatrix} -x_4 \\ y_4 \\ Z_{4x_4} \\ Z_{4y_4} \end{pmatrix} = \mathbf{t}_{41} \begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix};$$

$$\mathbf{t}_{11} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \mathbf{t}_{21} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \mathbf{t}_{31} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \mathbf{t}_{41} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

The matrices t_{ii} are operators which carry the space (x_1, $-y_1$, Z_{1x_1}, Z_{1y_1}) into any of its equivalents. They also represent simple permutation operators and can be written

$$\mathbf{t}_{11} = \mathbf{P}(I)E \qquad \mathbf{t}_{21} = \mathbf{P}(13)E \qquad \mathbf{t}_{31} = \mathbf{P}(24)E \qquad \mathbf{t}_{41} = \mathbf{P}(13)(24)E,$$

where E is the unit matrix ($\mathbf{t}_{11}$) and the P's are the permutations on the rows of E or the fundamental (1 space).

It can be readily verified that the $\mathbf{t}_{ii}$ represent an Abelian group t of transformations isomorphic with the four element permutation group $\mathbf{P}(1)(2)(3)(4)$; $\mathbf{P}(13)(2)(4)$; $\mathbf{P}(1)(3)(24)$; $\mathbf{P}(13)(24)$. These groups of operators transform the equivalent spaces characteristic to Z_1, Z_2, Z_3, Z_4 into each other. They have the multiplication tables:

	$\mathbf{t}_{11}$	$\mathbf{t}_{21}$	$\mathbf{t}_{31}$	$\mathbf{t}_{41}$
$\mathbf{t}_{11}$	I	$\mathbf{t}_{21}$	$\mathbf{t}_{31}$	$\mathbf{t}_{41}$
$\mathbf{t}_{21}$	$\mathbf{t}_{21}$	I	$\mathbf{t}_{41}$	$\mathbf{t}_{31}$
$\mathbf{t}_{31}$	$\mathbf{t}_{31}$	$\mathbf{t}_{41}$	I	$\mathbf{t}_{21}$
$\mathbf{t}_{41}$	$\mathbf{t}_{41}$	$\mathbf{t}_{31}$	$\mathbf{t}_{21}$	I

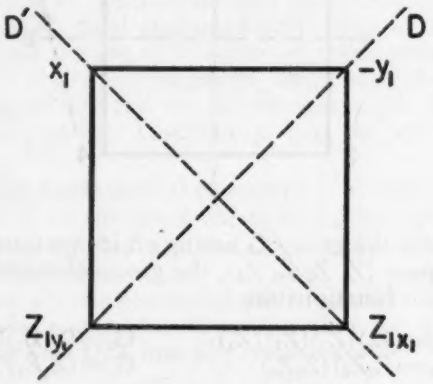
	P(I)	P(13)	P(24)	P(13)(24)
P(I)	I	P(13)	P(24)	P(13)(24)
P(13)	P(13)	I	P(13)(24)	P(24)
P(24)	P(24)	P(13)(24)	I	P(13)
P(13)(24)	P(13)(24)	P(24)	P(13)	I

Written in terms of the space $(x_1 - y_1\ Z_{1x_1}\ Z_{1y_1})$, the permutation group **g** contains the elements

$$\mathbf{g}_1 = (x_1)(-y_1)(Z_{1x_1})(Z_{1y_1}) \qquad \mathbf{g}_2 = (x_1 Z_{1x_1})(-y_1)(Z_{1y_1})$$

$$\mathbf{g}_3 = (x_1)(Z_{1x_1})(-y_1 Z_{1y_1}) \qquad \mathbf{g}_4 = (x_1 Z_{1x_1})(-y_1 Z_{1y_1})$$

This group is isomorphic to a group of permutations on the vertices of a square which leave the square invariant. In the figure



the transformations, $\mathbf{t}_{\alpha 1}$, or permutation operators, $\mathbf{g}_i$, have the following correspondence to the ordinary symmetry operations

$$\mathbf{g}_1 = \mathrm{I} \qquad \mathbf{g}_2 = \mathrm{D} \qquad \mathbf{g}_3 = \mathrm{D}' \qquad \mathbf{g}_4 = \mathrm{R}'',$$

where D, D′ are reflections in the diagonal planes, R″ is a rotation of 180°, and I is the identity operation (except for notation this group comprises the V, $-S$, $-P$, T part of figure 1(a), 1(g), 1(e), 1(c) of Koenig's paper).

If equations 1′, as a group, are considered in a standard form, then it is easily shown that this form remains invariant under the group of contact transformations, $\mathbf{t}_{41}$, provided the functions Z_1, Z_2, Z_3, Z_4, when they occur explicitly are subjected to the associated transformations

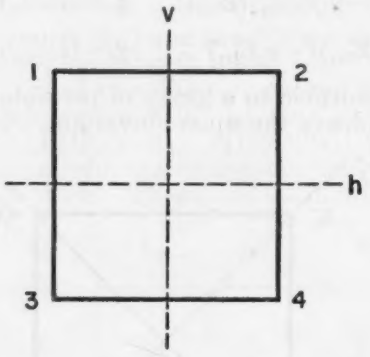
$$\begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix} = \mathbf{T}_{11}\begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix} \quad \begin{pmatrix} Z_2 \\ Z_1 \\ Z_4 \\ Z_3 \end{pmatrix} = \mathbf{T}_{21}\begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix} \quad \begin{pmatrix} Z_3 \\ Z_4 \\ Z_1 \\ Z_2 \end{pmatrix} = \mathbf{T}_{31}\begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix} \quad \begin{pmatrix} Z_4 \\ Z_3 \\ Z_2 \\ Z_1 \end{pmatrix} = \mathbf{T}_{41}\begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix}$$

$$\mathbf{T}_{11} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \mathbf{T}_{21} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \mathbf{T}_{31} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad \mathbf{T}_{41} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

These matrices represent permutation operators on the rows of the unit matrix, or on the space $(Z_1 \quad Z_2 \quad Z_3 \quad Z_4)$

$$\mathbf{T}_{11} \sim \mathbf{P}(1)(2)(3)(4) = \mathbf{G}_1 \qquad \mathbf{T}_{21} \sim \mathbf{P}(12)(34) = \mathbf{G}_2$$
$$\mathbf{T}_{31} \sim \mathbf{P}(13)(24) = \mathbf{G}_3 \qquad \mathbf{T}_{41} \sim \mathbf{P}(14)(23) = \mathbf{G}_4$$

The $\mathbf{T}_{i1}$ constitute an Abelian group isomorphic to the permutation group $\mathbf{G}$ composed of the $\mathbf{G}_i$. The square



is invariant under the group $\mathbf{G}$ acting on its vertices. Relabeling the figure for the space $(Z_1\ Z_2\ Z_3\ Z_4)$, the group elements of $\mathbf{G}$ in terms of the characteristic functions are

$$\mathbf{G}_1 = (Z_1)(Z_2)(Z_3)(Z_4) \qquad \mathbf{G}_2 = (Z_1Z_2)(Z_3Z_4)$$
$$\mathbf{G}_3 = (Z_1Z_3)(Z_2Z_4) \qquad \mathbf{G}_4 = (Z_1Z_4)(Z_2Z_3)$$

These elements correspond, in order, to the following symmetry operations:

I=Identity. $\qquad$ V=reflection in v.
H=Reflection in h. $\qquad$ R''=Rotation of 180°.

and have the multiplication table:

	$\mathbf{G}_1$	$\mathbf{G}_2$	$\mathbf{G}_3$	$\mathbf{G}_4$
$\mathbf{G}_1$	I	$\mathbf{G}_2$	$\mathbf{G}_3$	$\mathbf{G}_4$
$\mathbf{G}_2$	$\mathbf{G}_2$	I	$\mathbf{G}_4$	$\mathbf{G}_3$
$\mathbf{G}_3$	$\mathbf{G}_3$	$\mathbf{G}_4$	I	$\mathbf{G}_2$
$\mathbf{G}_4$	$\mathbf{G}_4$	$\mathbf{G}_3$	$\mathbf{G}_2$	I

The preceding results can be condensed into:

Theorem 1.—The fundamental equations 1′, remain invariant under the Contact Transformations defined by equations 2 and the associated group **G** on the Legendre transformation functions, provided absolute values are taken for the elements of all equivalent spaces $(x_i y_i Z_{1x_i} Z_{iy_i})$.

The restriction to absolute values can be removed if in applying **g** and **G** to equations 1′, numerator and denominator of the partial derivatives are transformed independently, that is, formally. This procedure eliminates the use of the contact transformations.

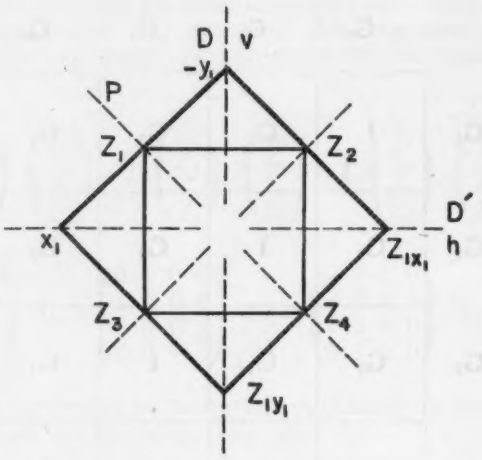
The spaces of **G** and **g** are exclusive, and hence the elements $\mathbf{G}_i\mathbf{g}_i$ constitute a group $\mathcal{G}$ for the combined space $(Z_1\ Z_2\ Z_3\ Z_4)(x_1\ -y_1\ Z_{1x_1}\ Z_{1y_1})$. Consequently, Theorem 1 can be written in greater generality:

Theorem 1′.—The fundamental equations 1′ are invariant under the substitution group $\mathcal{G}$ on the space $(Z_1\ Z_2\ Z_3\ Z_4)(x_1\ -y_1\ Z_{1x_1}\ Z_{1y_1})$.

In Theorem 1′, except for notation, $\mathcal{G}$ consists of elements S_1, S_3, S_5, S_7 of the Koenig group.

The group $\mathcal{G}$ can also be generated geometrically. It is only necessary to inscribe the square for **G** within that for **g** such that the symmetry planes v and D, b and D', coincide.

There results:



Writing out the fundamental equations 2 and associated contact transformations in the remaining coordinate systems, the following theorems are immediately evident.

Theorem 2.—The matrix operators, $\mathbf{T}_{ij}$ and $\mathbf{t}_{ij}$, which, acting on the function and coordinate space of one representation, transform the fundamental equations 2 to any other representation with invariant form, are independent of the coordinate system.

Theorem 3.—If $\mathbf{t}_{i1}$ denotes the matrix of a Contact Transformation in a given representation, then the corresponding transformation for any other representation is given by the transform $\mathbf{t}^{-1}\mathbf{t}_{i1}\mathbf{t}$ (or $\mathbf{t}\mathbf{t}_{i1}\mathbf{t}^{-1}$), where $\mathbf{t}$ corresponds to the contact transformation carrying the old to the new representation.

Theorem 4.—The permutation group $\mathscr{G}$, which leaves the fundamental equations 2 invariant is independent of the coordinate system. (Theorem 4 is a restatemet of theorem 2.)

The invariance of the four contact transformations (including the identity) defined by equations 1′ under the group of linear transformations, $\mathbf{t}_{i1}$ can be extended to invariance under the substitution group $\mathscr{G}$ provided a supplementary rule of signs is introduced. For general consistency a particular equation must transform into the same equation whether directly under the substitution operator $\mathscr{G}_i$ or as an element of a matrix equation under the corresponding $\mathbf{t}_{i1}$. The equation

$$Z_{2x_2}=x_1$$

transforms under $\mathbf{t}_{21}$ as an element of

$$\begin{pmatrix} -x_2 \\ -y_2 \\ Z_{2x_2} \\ Z_{2y_2} \end{pmatrix} = \mathbf{t}_{21} \begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix}$$

and therefore becomes

$$\mathbf{t}_{41}\begin{pmatrix} -x_2 \\ -y_2 \\ Z_{2x2} \\ Z_{2y2} \end{pmatrix} = \mathbf{t}_{41}\mathbf{t}_{21}\begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix} = \mathbf{t}_{31}\begin{pmatrix} x_1 \\ -y_1 \\ Z_{1x_1} \\ Z_{1y_1} \end{pmatrix} = \begin{pmatrix} x_3 \\ y_3 \\ Z_{3x_3} \\ Z_{3y_2} \end{pmatrix}$$

$$(Z_{2x_2} = x_1) \rightarrow (Z_{3x_3} = Z_{1x_1}).$$

Before the substitution operator $\mathscr{G}_4$ can be applied to the given equation, the left side must be transformed into the space characteristic of $\mathscr{G}$, that is, (1 space). Hence

$$\frac{\partial Z_2}{\partial x_2} = \frac{\partial(\mathbf{T}_{21}Z_1)}{\partial(\mathbf{t}_{21}x_1)} = \frac{\partial(\mathbf{G}_2 Z_1)}{\partial(-Z_{1x_1})} = x_1,$$

where $\mathbf{T}_{21}Z_1$ and $\mathbf{t}_{21}x_1$ denote the matrix transforms of Z_2 and x_2. Applying $\mathscr{G}_4$.

$$\mathscr{G}_4\left(\frac{\partial Z_2}{\partial x_2}\right) = \frac{\partial(\mathbf{G}_4\mathbf{G}_2)Z_1}{-\partial(\mathbf{g}_4 Z_{1x_1})} = \frac{\partial(\mathbf{G}_3 Z_3)}{-\partial x_1} = \frac{\partial Z_3}{-\partial x_1} = \frac{\partial Z_3}{-\partial x_3}$$

$$\mathscr{G}_4 x_1 = Z_{1x_1}$$

and consequently

$$\left(\frac{\partial Z_2}{\partial x_2} = x_1\right) \rightarrow \left(\frac{\partial Z_3}{-\partial x_3} = Z_{1x_1}\right).$$

which is incorrect in sign on the left side. This alternation in sign will always occur when the transform of x_i and its conjugate Z_{1x_i} differ in sign. Hence the rule:

Rule of Signs.—If x_i and Z_{ix_i} of a given space transform with opposite signs, then in transforming Z_{ix_i} by substitution, it must be replaced by $Z_{i|x_i|}$. If, of course, x_i and Z_{ix_i} transform with the same sign, then the rule is unnecessary, but if applied, will yield correct results, provided Z_{ix_i} always transforms positive. This is in fact the case. There results:

Theorem 5.—The Contact Transformations associated with the fundamental equations 2 in any coordinate system are invariant under the substitution group $\mathscr{G}$ characteristic of that coordinate system, provided Z_{ix_i} is replaced by $Z_{i|x_i|}$. (This is the origin of Koenig's Rule of Signs.)

If equations 1′ are invariant under an extended group $\mathscr{G}^*$, Lagranges' Theorem on the decomposition of a finite group insures the order of this group to be a multiple of the order of $\mathscr{G}$, that is, 4. The order of $\mathscr{G}^* \leqq 24$, the order of the complete symmetric group on four elements, and therefore $\mathscr{G}^*$ if it exists, must be of order 8 or 12. The group $\mathscr{G}^*$ will include $\mathscr{G}$ and its cosets $\mathscr{G}\,\mathbf{g}_i$ (or $\mathbf{g}_i\,\mathscr{G}$), where $\mathbf{g}_i = \mathbf{S}_i\mathbf{s}_i$ is an element of $\mathscr{G}^*$ not in $\mathscr{G}$ and $\mathbf{S}_i$, $\mathbf{s}_i$ operate on $(Z_1\,Z_2\,Z_3\,Z_4)$ and $(x_1—y_1\,Z_{1x_1}\,Z_{1y_1})$, respectively.

Examination of equations 1′ show the basic form to be invariant under the symmetry operator

$$\mathbf{g}' = (Z_1)(Z_4)(Z_2Z_3)(x_1 - y_1)(Z_{1x_1}Z_{1y_1})_1$$

which corresponds geometrically to reflection of the generating square in the plane $\mathbf{P}$ ($\mathbf{g}'$ corresponds to S_6 of Koenig's group). The elements of the coset $\mathcal{G}\mathbf{g}'$ are

$$\mathcal{G}_5 = \mathcal{G}_1\mathbf{g}' = (Z_1)(Z_4)(Z_2Z_3)(x_1 - y_1)(Z_{1x_1}Z_{1y_1})$$

$$\mathcal{G}_6 = \mathcal{G}_2\mathbf{g}' = (Z_1Z_2Z_4Z_3)(x_1 - y_1Z_{1x_1}Z_{1y_1})$$

$$\mathcal{G}_7 = \mathcal{G}_3\mathbf{g}' = (Z_1Z_3Z_4Z_2)(x_1Z_{y_1}Z_{x_1} - y_1)$$

$$\mathcal{G}_8 = \mathcal{G}_4\mathbf{g}' = (Z_1Z_4)(Z_2)(Z_3)(x_1Z_{1y_1})(-y_1Z_{1x_1})$$

They do not form a group and do not correspond to contact transformations. They may be considered as formal symmetry operators.

It is easily verified that the eight elements $\mathcal{G}_i$ constitute a group $\mathcal{G}'$ which leaves the generating square invariant. It is therefore isomorphic to the Octic Group and has the multiplication table:

	$\mathcal{G}_1$	$\mathcal{G}_2$	$\mathcal{G}_3$	$\mathcal{G}_4$	$\mathcal{G}_5$	$\mathcal{G}_6$	$\mathcal{G}_7$	$\mathcal{G}_8$
$\mathcal{G}_1$	$\mathcal{I}$	$\mathcal{G}_2$	$\mathcal{G}_3$	$\mathcal{G}_4$	$\mathcal{G}_5$	$\mathcal{G}_6$	$\mathcal{G}_7$	$\mathcal{G}_8$
$\mathcal{G}_2$	$\mathcal{G}_2$	$\mathcal{I}$	$\mathcal{G}_4$	$\mathcal{G}_3$	$\mathcal{G}_6$	$\mathcal{G}_5$	$\mathcal{G}_8$	$\mathcal{G}_7$
$\mathcal{G}_3$	$\mathcal{G}_3$	$\mathcal{G}_4$	$\mathcal{I}$	$\mathcal{G}_2$	$\mathcal{G}_7$	$\mathcal{G}_8$	$\mathcal{G}_5$	$\mathcal{G}_6$
$\mathcal{G}_4$	$\mathcal{G}_4$	$\mathcal{G}_3$	$\mathcal{G}_2$	$\mathcal{I}$	$\mathcal{G}_8$	$\mathcal{G}_7$	$\mathcal{G}_6$	$\mathcal{G}_5$
$\mathcal{G}_5$	$\mathcal{G}_5$	$\mathcal{G}_7$	$\mathcal{G}_6$	$\mathcal{G}_8$	$\mathcal{I}$	$\mathcal{G}_3$	$\mathcal{G}_2$	$\mathcal{G}_4$
$\mathcal{G}_6$	$\mathcal{G}_6$	$\mathcal{G}_8$	$\mathcal{G}_5$	$\mathcal{G}_7$	$\mathcal{G}_2$	$\mathcal{G}_4$	$\mathcal{I}$	$\mathcal{G}_3$
$\mathcal{G}_7$	$\mathcal{G}_7$	$\mathcal{G}_5$	$\mathcal{G}_8$	$\mathcal{G}_6$	$\mathcal{G}_3$	$\mathcal{I}$	$\mathcal{G}_4$	$\mathcal{G}_2$
$\mathcal{G}_8$	$\mathcal{G}_8$	$\mathcal{G}_6$	$\mathcal{G}_7$	$\mathcal{G}_5$	$\mathcal{G}_4$	$\mathcal{G}_2$	$\mathcal{G}_3$	$\mathcal{I}$

The general result can be incorporated in theorem 6.

Theorem 6.—The form of the fundamental equations 1′ is invariant under the group $\mathscr{G}^*$, and this group is the largest permutation group having this property.

An additional proof that $\mathscr{G}^*$ is the largest permutation group which preserves the standard form lies in the fact that the Octic Group is the largest permutation group under which the bilinear form $(x_1+x_2-x_3-x_4)^2$ is invariant. The last of equations 1′ can be written

$$(Z_1+Z_4-Z_2-Z_3)^2=0,$$

and this must be true under all transformations. Except for notation, this is the bilinear form invarient under the Octic Group. Hence the theorem.

The matrix representatives of the new operators $\mathbf{g}_5 \ldots \mathbf{g}_8$ are

$$\mathbf{t}_{51}=\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}\quad \mathbf{t}_{61}=\begin{pmatrix}0&1&0&0\\0&0&1&0\\0&0&0&1\\1&0&0&0\end{pmatrix}\quad \mathbf{t}_{71}=\begin{pmatrix}0&0&0&1\\1&0&0&0\\0&1&0&0\\0&0&1&0\end{pmatrix}\quad \mathbf{t}_{81}=\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix},$$

which taken with those representing $\mathbf{g}_1 \ldots \mathbf{g}_4$ for a group $\mathbf{t}^*$ having a multiplication table in 1–1 correspondence with that of $\mathscr{G}^*$ Contact transformations are transformed under these operators exactly as previously described. For example, the transformation defined by equations 2a is transformed by $\mathscr{G}_6$ into

$$t_{61}\begin{pmatrix}2\\\text{space}\end{pmatrix}=t_{21}t_{61}\begin{pmatrix}1\\\text{space}\end{pmatrix}=t_{51}\begin{pmatrix}1\\\text{space}\end{pmatrix},$$

which is equivalent to

$$t_{31}\begin{pmatrix}2\\\text{space}\end{pmatrix}=\begin{pmatrix}4\\\text{space}\end{pmatrix}$$

the contact transformation characteristic of Z_4 expressed in the coordinates of (2 space). Similar results are obtained for other operators. The general result is contained in theorem:

Theorem 7.—The Contact Transformations defined by equations 2 are invariant under the group $\mathbf{t}^*$ of elements $\mathbf{t}_{i1}$ $i=1 \ldots 8$.

The preceding theorems can now be extended to the larger groups. Thus:

Theorem 2′.—The matrix groups $\mathbf{T}^*$ and $\mathbf{t}^*$, under which the fundamental equations 1′ are invariant, are independent of the representation.

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Theorem 4′.—The permutation group $\mathcal{G}^*$ which leaves the fundamental equations 1′ invariant is independent of the representation.

Theorem 5′.—The Contact Transformations associated with the fundamental equations 2 in any representation are invariant under the substitution group $\mathcal{G}^*$ characteristic of that representation provided Z_{ix_i} is replaced by $Z_i|_{x_i}$.

A consequence of the invariance of the contact transformations under the substitution group $\mathcal{G}^*$ is the existence of characteristic families of equations also invariant under $\mathcal{G}^*$. Families having important correlatives in general thermodynamic theory are contained in the following theorems. Given an equation of the form expressed in the theorem, the group $\mathcal{G}^*$ generates the entire family, provided the contact transformations themselves are employed to reduce the symbolism.

Theorem 8.—The family of four differential forms

$$Z_i-\left(\frac{\partial Z_i}{\partial x_i}\right)_{y_i}dx_i-\left(\frac{\partial Z_i}{\partial x_i}\right)_{x_i}dy_i=0$$

is invariant under the substitution group $\mathcal{G}^*$.

Theorem 9.—The eight member family of the form

$$\left(\frac{\partial Z_i}{\partial x_i}\right)_{y_i}=-x_j$$

is invariant under the group $\mathcal{G}^*$.

Theorem 10.—The four equations of the form

$$\left(\frac{\partial Z_i}{\partial x_i}\right)_{y_j}=\left(\frac{\partial Z_i}{\partial x_j}\right)_{y_i}$$

constitute a family invariant under the characteristic group $\mathcal{G}^*$.

Theorem 11.—The family of eight identities

$$\frac{\partial^2 Z_i}{\partial x_i \partial y_i}=\frac{\partial^2 Z_i}{\partial y_i \partial x_i}$$

is invariant under $\mathcal{G}^*$.

The invariance of the fundamental equations yields theorems 12, 13, and 14:

Theorem 12.—The family of eight equations of the form

$$Z_i=Z_j-x_j-\left(\frac{\partial Z_j}{\partial x_j}\right)_{y_j}$$

is invariant under the group $\mathcal{G}^*$.

Theorem 13.—The four equations of the form

$$Z_i=Z_j-x_j\left(\frac{\partial Z_j}{\partial x_j}\right)_{y_j}-y_j\left(\frac{\partial Z_j}{\partial y_j}\right)_{x_j}$$

constitute a family invariant under the group $\mathcal{G}^*$.

Theorem 14.—The equation

$$(Z_1+Z_4)-(Z_2+Z_3)=0$$

invariant under the group $\mathscr{G}^*$.

Other families of formulas invariant under $\mathscr{G}^*$ are deducible from the fundamental equations 1′ by the application of operators such as $\partial/\partial x$, $\partial/\partial y$, d.

The transform of a formula obtained by applying the operator $\mathbf{O}$ to one of the fundamental equations is derived by applying the group operator $\mathbf{g}_i$ to both $\mathbf{O}$ and f in the equation

$$\mathbf{O}f=0.$$

For example, from the equation

$$Z_1=Z_3-y_3\left(\frac{\partial Z_3}{\partial y_3}\right)_{x_3}$$

or

$$Z_1-Z_3+y_3\left(\frac{\partial Z_3}{\partial y_3}\right)_{x_3}=0,$$

the operator $\partial/\partial x_3$ yields

$$\frac{\partial}{\partial x_3}\left\{Z_1-Z_3+y_3\left(\frac{\partial Z_3}{\partial y_3}\right)_{x_3}\right\}=0,$$

and the substitution operator $\mathscr{G}_7$ gives

$$\frac{\partial}{\partial(\mathbf{t}_{71}x_3)}\mathscr{G}_7\left\{Z_1-Z_3+y_3\left(\frac{\partial Z_3}{\partial y_3}\right)_{x_3}\right\}=0,$$

where the transform $\mathbf{t}_{71}x_3$ is obtained from the matrix equation

$$\binom{3}{\text{space}}\rightarrow\mathbf{t}_{31}\mathbf{t}_{71}\binom{1}{\text{space}}=\mathbf{t}_{51}\binom{4}{\text{space}},$$

so that

$$\frac{\partial}{\partial x_3}\rightarrow\frac{\partial}{\partial y_4},$$

and the transformed equation becomes:

$$\frac{\partial}{\partial y_4}\left\{Z_3-Z_4+x_4\left(\frac{\partial Z_4}{\partial x_4}\right)_{y_4}\right\}=0.$$

The reversal in order of the product of the matrices $\mathbf{t}_{71}$ and $\mathbf{t}_{31}$ in the transform follows from the fact that $\mathscr{G}^*$ is non-Abelian and that $\mathscr{G}^*$ is written in terms of (1 space). This method yields theorem 15.

Theorem 15.—Equations of the form

$$\left(\frac{\partial Z_i}{\partial y_j}\right)_{x_i}-\left(\frac{\partial Z_k}{\partial y_l}\right)_{x_l}=-y_j\left\{\left(\frac{\partial^2 Z_j}{\partial y_i^2}\right)_{x_i}-\left(\frac{\partial^2 Z_l}{\partial y_i^2}\right)_{x_l}\right\}=-y_j\left\{\frac{\partial^2 Z_j}{\partial x_i\partial y_i}\frac{\partial^2 Z_l}{\partial x_i\partial y_j}\right\}$$

constitute a four-member family invariant under the substitution group $\mathscr{G}^*$.

Theorem 16.—The eight equations of the form

$$\left(\frac{\partial Z_i}{\partial y_j}\right)_{x_i}=-y_i\left(\frac{\partial^2 Z_j}{\partial y_j^2}\right)_{x_i}$$

comprise a family invariant under the substitution group $\mathscr{G}^*$.

Theorem 17.—The eight member family of form

$$\left(\frac{\partial y_i}{\partial x_i}\right)_{Z_j} = -\left(\frac{\partial Z_j}{\partial x_i}\right)_{y_i} \Big/ \left(\frac{\partial Z_j}{\partial y_i}\right)_{x_i}$$

$$= -\frac{\left\{\left(\frac{\partial Z_i}{\partial x_i}\right)_{y_i} - y_i \frac{\partial}{\partial x_i}\left(\frac{\partial Z_i}{\partial y_i}\right)_{x_i}\right\}}{\left(\frac{\partial Z_j}{\partial y_i}\right)_{x_i}}$$

is invariant under the substitution group $\mathcal{G}^*$.

Transformation formulas for the second derivatives can be obtained by elementary calculation from the four sets of Contact Transformations corresponding to the four equivalent representations. They give the following theorems:

Theorem 18.—The eight equations of the type

$$Z_{jx_jx_j} = \frac{-1}{Z_{ix_ix_i}}$$

form a family invariant under the substitution group $\mathcal{G}^*$.

Theorem 19.—The family of eight equations of form

$$Z_{jx_jy_j} = \frac{-Z_{ix_iy_i}}{Z_{ix_ix_i}}$$

is invariant under the substitution group $\mathcal{G}^*$, provided the following Rule of Signs is applied.

Rule.—The conjugates Z_{ix_i}, Z_{iy_i} must be taken with absolute signs wherever they occur in the transform of x_j, y_j in the basic form. $\mathcal{G}^*$ is expressed in (1 space).

Theorem 20.—The eight equations of form

$$-Z_{jy_jy_j} = \frac{Z^2_{ix_iy_i} - Z_{ix_ix_i}Z_{iy_iy_i}}{Z_{ix_ix_i}}$$

constitute a family invariant under the substitution group $\mathcal{G}^*$.

Theorem 21.—Equations of the form

$$Z_{jx_jx_j} = \frac{Z_{iy_iy_i}}{Z^2_{ix_iy_i} - Z_{ix_ix_i}Z_{iy_iy_i}}$$

constitute an eight membered family invariant under the substitution group *.

Theorem 22.—The four equations of the type

$$Z_{jx_jy_j} = \frac{Z_{ix_iy_i}}{Z^2_{ix_iy_i} - Z_{ix_ix_i}Z_{iy_iy_i}}$$

form a family invariant under the substitution group $\mathcal{G}^*$, provided the Rule of Signs given in Theorem 19 is applied.

The Legendre transformation functions characteristic of a given representation are simply related to Lie's [4] theory of a "group of

functions." A set of n functions $v_1 \ldots v_n$ constitute a group of order n if they satisfy the two conditions:

1. v_i are algebraically independent.
2. Every combination $(v_i v_j)$ of the set is expressible in terms of the set and

$$(v_i v_j) = \sum_k \left(\frac{\partial v_i}{\partial x_k} \frac{\partial v_j}{\partial p_k} - \frac{\partial v_i}{\partial p_k} \frac{\partial v_j}{\partial x_k} \right).$$

Any other function u which has the property that all $(v_i u)$ are expressible in terms of the v_i belongs to the group. If all the $(v_i u)$ are zero, then u is said to be in involution to the group and is called an indicial function (ausgezeichnete Funktion) of the group.

Lie [5] has given a number of theorems on the properties of a group of functions of which the two following are of particular interest in connection with the preceding results.

Theorem 25L.—A group of functions in the variables x_i, p_i possesses only two properties which are invariant under all contact transformations of the form

$$Z' = Z + \Omega(xp) \qquad x_i' = X_i(xp) \qquad p_i' = P_i(xp).$$

The first is the order of the group and the second the number of independent indicial functions of the group.

Theorem 26L.—If the r independent functions $U_1 \ldots U_r$ in the variables $x_1 \ldots x_n$, $p_1 \ldots p_n$ form a group of functions of order r, and the functions $V_1 \ldots V_r$ in the variables $x_1' \ldots x_n'$, $p_1' \ldots p_n'$ likewise a group of order r, then there exists a contact transformation of the form

$$Z' = Z + \Omega(xp) \qquad x_i' = X_i(xp) \qquad p_i' = P_i(xp),$$

transforming $U_1 \ldots U_r$ into the corresponding $V_1 \ldots V_r$, if and only if, every combination $(U_i U_j)$ is expressed in terms of $U_1 \ldots U_r$ in the same way as the corresponding $(V_i V_j)$ in terms of the $V_1 \ldots V_r$.

It is easily verified that each of the sets of Legendreian functions:

Z_2	Z_1	Z_4	Z_2
Z_3	Z_4	Z_1	Z_3
Z_4	Z_3	Z_2	Z_1

characteristic of the fundamental equations 1′ in the four equivalent representations, constitute a group of functions according to the Lie definition. Each group is of order three and possesses one indicial function. They are

$$f_1 = \frac{Z_3 - Z_2}{Z_4 - Z_2} \qquad f_2 = \frac{Z_4 - Z_1}{Z_3 - Z_1} \qquad f_3 = \frac{Z_1 - Z_4}{Z_2 - Z_4} \qquad f_4 = \frac{Z_2 - Z_3}{Z_1 - Z_3},$$

and the set can be generated by the substitution group **G** on any one of them. Hence theorem 23.

Theorem 23.—The indicial functions associated with the group of Legendreian functions characteristic of the four representations constitute a four member family invariant under the substitution subgroup **G** of $\mathcal{G}^*$.

An elementary calculation shows that each of the characteristic sets given above satisfies the conditions of Lie's Theorem 26, and hence are transformable into each other by a cylindrical tangential transformation. The transformations in the representation of (1 space) are those given in equations 2. The equivalent transformations in any other representation can be obtained by applying Theorem 3.

VI. THERMODYNAMIC FORMULAS

If the following correspondences are made, the preceding results are directly interpretable as general thermodynamic relations.

$$Z_1=E \qquad Z_2=H \qquad Z_3=F \qquad Z_4=G$$

$$(x_1,y_1)=(V,S) \qquad (x_3,y_3)=(x_1,Z_{1y_1})=(V,T)$$

$$(x_2,y_2)=(-Z_{1x_1},y_1)=(P,S) \qquad (x_4,y_4)=(x_2,y_3)=(P,T)$$

Under this correspondence equations 1′ transform into the fundamental equations 1 and the group $\mathcal{G}^*$ becomes identical with the Koenig substitution group in the representation of (1 space). The generating square coincides with figure 1(a) of Koenig's paper.

The generation of a family of formulas by the action of the substitution $\mathcal{G}^*$ on a basic form is of course subject to the rules of signs given in the preceding section. Moreover, since a family of formulas can be expressed either in terms of the thermodynamic functions and their derivatives, or in a reduced form in terms of V, S, P, T and E, H, F, G, the application of a rule will be determined by the character of the basic form. The general result can be expressed in the theorems:

Theorem 24.—If a basic form is deducible from the fundamental equations 1, or equivalent in another representation, by the action of an operator **O** followed by algebraic rearrangement, the substitution group $\mathcal{G}^*$ generates an invariant family of 1, 2, 4, or 8 members.

Theorem 25.—If a basic form of Theorem 24 is transformed by the use of the equations of the contact transformations, then the substitution group $\mathcal{G}^*$ generates an invariant family of 1, 2, 4, or 8 members, provided one of each conjugate pair of variables in every term of the new basic form is enclosed in the absolute sign.

The following table is a condensation of the theorems given in the preceding section on families of equations invariant under the substitution group $\mathcal{G}^*$.

Origin	Order of family	Equivalent basic forms
Theorem 8	4	$dE-\left(\frac{\partial E}{\partial V}\right)_S dV-\left(\frac{\partial E}{\partial S}\right)_V dS=0$
		$dE+\lvert P\rvert dV-\lvert T\rvert dS=0$
Theorem 9	8	$\left(\frac{\partial E}{\partial \lvert V\rvert}\right)_S=-P.$

Origin	Order of family	Equivalent basic forms
Theorem 10	4	$\left(\frac{\partial E}{\partial V}\right)_S=\left(\frac{\partial F}{\partial V}\right)_T$
Theorem 11	8	$\frac{\partial^2 E}{\partial V \partial S}=\frac{\partial^2 E}{\partial S \partial V}$ $\left(\frac{\partial T}{\partial \lvert V\rvert}\right)_S=-\left(\frac{\partial P}{\partial \lvert S\rvert}\right)_V$
Theorem 12	8	$H=E-V\left(\frac{\partial E}{\partial V}\right)_S$ $H=E+\lvert P\rvert V$
Theorem 13	4	$G=E-V\left(\frac{\partial E}{\partial V}\right)_S-S\left(\frac{\partial E}{\partial S}\right)_V$ $G=E+\lvert P\rvert V-\lvert T\rvert S$
Theorem 14	1	$(E+G)-(H+F)=0.$
Theorem 15	4	$\left(\frac{\partial H}{\partial T}\right)_P-\left(\frac{\partial E}{\partial T}\right)_V=-T\left[\left(\frac{\partial^2 G}{\partial T^2}\right)_P-\left(\frac{\partial^2 F}{\partial T^2}\right)_V\right.$ $=-T\frac{\partial^2 G}{\partial T \partial P}\frac{\partial^2 F}{\partial T \partial V}$ $=T\left(\frac{\partial \lvert V\rvert}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$
Theorem 16	8	$\left(\frac{\partial H}{\partial T}\right)_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ $=T\left(\frac{\partial \lvert S\rvert}{\partial T}\right)_P$

Origin	Order of family	Equivalent basic forms
Theorem 17	8	$\left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial E}{\partial V}\right)_T \Big/ \left(\frac{\partial E}{\partial T}\right)_V$
		$= -\frac{\left\{\left(\frac{\partial F}{\partial V}\right)_T - T\frac{\partial^2 F}{\partial V \partial T}\right\}}{\left(\frac{\partial E}{\partial T}\right)_V}$
		$\left(\frac{\partial T}{\partial \lvert V\rvert}\right)_E = \frac{P - T\left(\frac{\partial P}{\partial T}\right)}{\left(\frac{\partial E}{\partial T}\right)_V}$
Theorem 18	8	$\left(\frac{\partial H^2}{\partial P^2}\right)_S = -\frac{1}{\left(\frac{\partial^2 E}{\partial V^2}\right)_S}.$
Theorem 19	8	$\frac{\partial^2 H}{\partial S \partial \lvert P\rvert} = -\frac{\frac{\partial^2 E}{\partial V \partial S}}{\left(\frac{\partial^2 E}{\partial V^2}\right)_S}.$
Theorem 20	8	$-\left(\frac{\partial^2 H}{\partial S^2}\right)_P = \frac{\frac{\partial^2 E}{\partial V \partial S} - \left(\frac{\partial^2 E}{\partial V^2}\right)_S \left(\frac{\partial^2 E}{\partial S^2}\right)_V}{\left(\frac{\partial^2 E}{\partial V^2}\right)_S}.$
Theorem 21	8	$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \frac{\left(\frac{\partial^2 E}{\partial S^2}\right)_V}{\left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 - \left(\frac{\partial^2 E}{\partial V^2}\right)_S \left(\frac{\partial^2 E}{\partial S^2}\right)_V}.$
Theorem 22	4	$\frac{\partial^2 G}{\partial \lvert P\rvert \partial \lvert T\rvert} = \frac{\frac{\partial^2 E}{\partial V \partial S}}{\left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 - \left(\frac{\partial^2 E}{\partial V^2}\right)_S \left(\frac{\partial^2 E}{\partial S^2}\right)_V}.$

There are of course several equivalent expressions for a basic form involving second-order derivatives of the thermodynamic functions when expressed in terms of V, S, T, P. Since this paper is not concerned with providing a catalog of all such formulas they have been omitted. In fact, from the theoretical point of view, all formulas should remain implicitly contained in the general relations between the thermodynamic functions and their derivatives. Such a procedure would effect a considerable condensation of necessary formulas without entailing excessive effort in the deduction of a required relation.

Relations connecting the second-order derivatives of V, S, T, P, can be deduced from transformation formulas for the third-order derivatives of the characteristic functions. The relations are not complex, but there are many of them. In light of the results of this study, it is very probable that these equations can be grouped into families invariant under the substitution group $\mathscr{G}^*$, thereby eliminating an extensive catalog of formulas.

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